

FINAL PLAN

LOMPOC PESTICIDE AIR MONITORING
MULTIPLE-PESTICIDE SAMPLING AND ANALYSIS PLAN
September 2000

PREPARED BY
THE CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
DEPARTMENT OF PESTICIDE REGULATION

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**California Environmental Protection Agency
Department of Pesticide Regulation**

Executive Summary
Lompoc Pesticide Air Monitoring
Multiple-Pesticide Sampling and Analysis Plan

What is the purpose of the air sampling that the Department of Pesticide Regulation (DPR) plans to conduct?

The Department of Pesticide Regulation (DPR) plans to measure air concentrations of as many of the pesticides as possible listed in Tables 1 and 2, depending on methods development. These pesticides will be monitored during the spring, summer, and fall. Using multiple-pesticide analysis of single samples, this sampling and analysis plan is designed to measure concentrations of these pesticides for three to ten weeks. DPR will then use the measured data to determine if acute and subchronic screening levels have been exceeded. The design is to collect data for acute and subchronic exposures, not chronic exposures; however, DPR will qualitatively compare data to chronic screening levels. (Note: Acute exposure is an exposure for a short time, usually 24 hours or less. Subchronic exposure is an exposure for an intermediate period of time, generally one to three months. Chronic exposure is an exposure for extended periods of time, usually for a significant portion of a lifetime.)

The study is part of a two-phase monitoring program to measure pesticide air concentrations in the Lompoc area. The primary objective of the two-phase pesticide air monitoring program is to gather information to answer three main questions: (1) Are Lompoc residents exposed to pesticides in air? (2) If so, which pesticides, and in what amounts? (3) Do these levels exceed human health standards?

Why is DPR conducting this air sampling?

In 1997, DPR formed the Lompoc Interagency Work Group (LIWG) to help investigate residents' concerns first voiced in 1992 about potential pesticide exposure from drift of pesticides during and following agricultural applications. The LIWG is composed of staff from federal, state, and county agencies as well as community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air monitoring program, and to consider potential exposures from environmental factors, such as crystalline silica, radon, meteorological conditions, and pollen and mold. Other agencies plan to do, or have done, monitoring to measure levels of crystalline silica, radon, and meteorological conditions.

The pesticide exposure subgroup (now called the Technical Advisory Group) developed a work plan that recommended comprehensive air monitoring in Lompoc during the growing season to investigate potential pesticide exposure to residents from pesticides applied to agricultural fields that may migrate by air to adjacent residential areas. This subgroup developed a list of priority pesticides, 12 of which were tested for in 1998 (see Phase 1 below, Table 3).

The Governor's 1999-2000 budget allocated funds to DPR for monitoring pesticide air concentrations in the spring, summer, and fall 2000 in Lompoc. This document describes the monitoring planned for pesticides during the months of late May through early August (Table 1) and in September 2000 (Table 2) using multiple-pesticide analysis of single samples. DPR plans to sample for up to 23 pesticides and 5 breakdown products (Table 1) during late May through early August. University of California Davis' Trace Analytical Laboratory (UCD) has developed methods to analyze these samples. In September, DPR will collect and analyze samples for as many of the compounds listed in Table 2 as methods development allows. Battelle's Atmospheric Science and Applied Technology Department (Batelle) is in the process of developing analytical methods for the chemicals listed in Table 2.

What other pesticide air sampling has DPR done in Lompoc?

For four weeks during August and September 1998, DPR conducted a monitoring study that was intended to test pesticide sampling and analysis methods and to determine if a subset of the total pesticides in use in the area could be measured in air (Phase 1). With some exceptions, these goals were achieved. This test study provided the basis for the multiple-pesticide sampling and analysis approach this plan follows. However, due to the limited nature of the 1998 sampling, these results are not appropriate for risk assessment. For more information about this sampling, go to our website at <www.cdpr.ca.gov>, click on Programs and Services, then Lompoc Project, Update on Lompoc, "Phase 1 Results."

Phase 2 consists of two sampling and analysis projects. In addition to the multiple-pesticide sampling and analysis, the other part of this second phase is sampling and analysis for fumigants, a subset of pesticides whose use has historically been highest in fall and winter. DPR collected samples for that project in January and February 2000 and will collect the remainder in fall/winter 2000. For more information, go to our website at <www.cdpr.ca.gov>, click on Programs and Services, then Lompoc Project to find DPR's "Lompoc Pesticide Air Monitoring Fumigant Sampling and Analysis Plan."

How were the pesticides selected?

Since few methods exist at this time for air monitoring where single samples can be collected and analyzed for multiple pesticides at the low concentrations required to estimate inhalation exposure, methods development work was required to most efficiently use available resources to monitor as many pesticides of potential concern as possible. During this past year, the TAG reviewed the pesticides used in Lompoc (1996-1998), developed a ranking scheme based on the most current information for use, toxicity, and vapor pressure (volatility), and prioritized the chemicals for which to request methods development (Table 3). This list was further refined, eliminating chemicals due to analytical difficulties or low toxicity. The TAG then identified potential laboratories (UCD and Battelle) to develop methods for and conduct multi-pesticide analysis of single samples. Tables 1 and 2 show the final lists of prioritized candidate compounds.

How many sites will DPR monitor and where will the sites be located?

Ambient air monitoring will be conducted at four sites within the city limits of Lompoc.

DPR based its site selection primarily on proximity to agricultural area, wind patterns, and U.S. Environmental Protection Agency (U.S. EPA) siting criteria. Three of the four air sampling sites were selected based on nearness to pesticide application sites and predominant wind patterns during that time of year. The fourth site, near the center of Lompoc, was selected to be representative of pesticide concentrations that might be found closer to the center of the city.

What is the sample collection plan?

Pesticides will be monitored in two groups. One group of pesticides will be monitored late May through early August (Table 1), historically months when their use has been higher than other months in the year. Ambient air samples will be 24 hours in duration, collected four days per week for 10 consecutive weeks. The other group (Table 2) will be monitored during September when their use has been historically high. Samples will be 24 hours in duration, collected four days per week for three consecutive weeks.

What air sampling methods will be used?

Sorbent cartridges with XAD-4 resin will be used to collect air samples. Samples will be stored on dry ice and then delivered to the analyzing laboratory. UCD will analyze samples collected in late May to early August to measure concentrations of compounds listed in Table 1, and Battelle will analyze the samples collected in September to measure concentrations of the compounds listed in Table 2, using methods each of these laboratories has developed (or is in the process of developing) as part of this project.

What quality assurance and quality control procedures will be used?

To ensure sample validity and quality, appropriate quality control and quality assurance procedures will be used along the entire sampling and analysis process: in the field, during sample collection and storage, and in the laboratory during sample analysis. In addition, an independent, multi-agency quality assurance team will audit the laboratories participating in this study.

What are DPR screening levels?

Since enforceable human health standards for ambient air concentrations for these pesticides do not exist, DPR and a subcommittee of the LIWG's TAG plan to develop final health screening levels for these pesticides to place results in a health-based context.

The TAG has developed preliminary screening levels. These preliminary screening levels were generated using generally conservative assumptions to ensure that the analytical methods' detection limits will be lower than the final health screening levels (Tables 1 and 2).

Although not regulatory standards, DPR will use final health screening levels to evaluate the results and take actions as needed. Published U.S. EPA risk assessments will be used as the basis for these final screening levels. In addition, completed DPR risk assessments, in the form of Risk Characterization Documents, will be used. These final health screening levels are not legal health standards and should not be viewed as such. The final health screening levels represent the first tier in a risk evaluation and provide a

context in which to view measured levels of the pesticides monitored in this project.

What are the lowest levels of pesticide air concentrations that these methods detect?

The lowest preliminary screening level is 20 nanograms per cubic meter (ng/m³) (Tables 1 and 2). The 1998 test study (Phase 1) maximum air concentrations of the quantifiable samples for the pesticides that will also be monitored in this plan ranged from 5.3 to 760 ng/m³. UCD has predicted estimated quantitation limits of 3 to 9 ng/m³ for the compounds listed in Table 1; Battelle has predicted estimated quantitation limits of 5 ng/m³ for the compounds listed in Table 2.

What actions will DPR take based on the results?

Acute exposure: If the maximum 24-hour air concentration at any site is significantly below the final acute health screening level, no immediate action will be taken. If the maximum 24-hour air concentration is below the screening level, but not significantly below it, DPR may still consider further analysis (e.g., further monitoring, and/or a more detailed analysis of the health effects data). However, if the maximum 24-hour air concentration is greater than the final acute health screening level, then DPR will respond immediately with interim regulatory action or the development of a plan for further analysis, or both. Regulatory actions could consist of one or more of the following: permit conditions for restricted materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study.

Subchronic exposure: If the maximum two-week (i.e., 4 days/week x 2 weeks = 8 samples, collected on 8 days) average air concentration is significantly below the screening level, no immediate action will be taken. If the maximum two-week average air concentration is below the screening level, but not significantly below it, DPR may consider further analysis (e.g., further monitoring, and/or a more detailed analysis of the health effects data). If the maximum two-week average air concentration is greater than the final subchronic health screening level, then DPR will respond immediately with interim regulatory action or the development of a plan for further analysis, or both. Regulatory actions could consist of one or more of the following: permit conditions for restricted materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study.

Chronic exposure: If the estimated annual average concentration is below the final chronic health screening level, no immediate action will be taken. If the estimated annual average air concentration is above the screening level, DPR will conduct further analysis (e.g., further monitoring, and/or a detailed analysis of the health effects data).

What the sampling and analysis plan can and cannot do.

The goal of the sampling and analysis plan is to provide data to answer questions about the highest concentrations of these pesticides that occur over a short period of time. However, we will have no way of ensuring that we have monitored the “highest”

concentrations (e.g., the highest concentration of a pesticide could occur on a day we do not monitor) or under worst-case conditions (for similar reasons). Toxicologists use these values to determine potential exposure and to characterize the risk from these exposures. These data will be used to assess the risk to human health due to acute and subchronic exposures. However, this sampling and analysis plan has not been designed to answer questions about chronic exposures to these pesticides, but will provide a starting point for further analysis.

For a variety of reasons (e.g., meteorological conditions, location of applications relative to air samplers), maximum concentrations may occur at times other than when monitoring occurs. However, DPR will compare the monitoring results at different sites with daily pesticide use and meteorology data to assess the representativeness of the data.

The plan will provide information to estimate inhalation exposure; however, community exposure to pesticides by ingestion, dermal absorption, or other potential routes will not be measured. For these pesticides, the major route of exposure is expected to be through inhalation.

Some concentrations of pesticides may be too low to quantify given the current state of technology for chemical analysis. Data below the limit of quantitation will be reported as trace levels. Data below the method detection limit will be reported as none detected. However, when used for calculations (e.g., calculations of average concentrations), data below the limit of quantitation will be set equal to the mid-point between the limit of quantitation and the method detection limit while results below the method detection limit will be set equal to one-half the method detection limit.

The multiple-pesticide analysis of single samples will allow for identification and quantification of the pesticides listed in Tables 1 and 2, for which analytical methods have been developed. (Note: UCD has developed methods for all compounds in Table 1; Battelle soon will begin work on compounds listed in Table 2 and plans to develop methods for as many of them as possible.) However, the analysis may show compounds that are not on these lists. It is beyond the scope of this project to routinely identify compounds that are not listed in Tables 1 or 2.

Following applications, pesticides (other than those applied as dusts) move away from the target field by drift and post-application volatilization in two forms: gaseous and adsorbed onto airborne particulates. This monitoring study does not address this latter component. However, although the sample analysis does not account for all the particulate, we believe that the fraction we may be missing is a small percentage. Samples for particulates may be collected to estimate the missing fraction.

The U.S. EPA is currently developing methods to address the risks from exposure to multiple pesticides. These and/or other methods will be used in an effort to evaluate multiple pesticide exposure, in addition to the pesticide-by-pesticide evaluation.

When will the report be completed?

In an effort to have data be as complete and accurate as possible, and to ensure adequate time for all appropriate review and comment, it is not possible to specify a time the final report will be completed. However, DPR anticipates that these steps will be completed in time to release a final report by the end of 2001.

For a complete copy of the sampling and analysis plan or for more information about this project, please contact Randy Segawa in writing at the Environmental Monitoring and Pest Management Branch of DPR, by telephone at (916) 324-4137, or by e-mail at <rsegawa@cdpr.ca.gov>. To view the entire plan, see DPR's home page at www.cdpr.ca.gov, and look under Programs and Services, Lompoc Project.

Table 1. Group 1—List of Candidate Compounds for a Multi-residue Air Sampling Scheme (analysis by gas chromatography at UCD). Monitoring is planned for late May through early August 2000.

Pesticide (Active Ingredient)	Breakdown product	Detection Limit (ng/m³)	Limit of Quantitation (ng/m³)	Preliminary Screening level (ng/m³)
Chlorpyrifos	Chlorpyrifos oxon	0.76	4	1,000
Chlorthal-dimethyl		0.28	1	4,700
Chlorothalonil		1.4	7	2,300
Cycloate		1.8	9	16,000
Diazinon	Diazinon oxon	0.72	4	300
Dicloran		1.3	6	82,000
Dicofol		1.3	7	3,900
Dimethoate	Dimethoate oxon	0.56	3	330
EPTC		0.62	3	41,000
Ethalfuralin		0.60	3	79
Fonofos	Fonofos oxon	0.66	3	6,600
Iprodione		1.5	8	160
Malathion	Malathion oxon	0.82	4	4,600
Mefenoxam		0.60	3	200,000
Metolachlor		0.58	3	250,000
Naled		0.96	5	6,600
Oxydemeton-methyl*				410
PCNB		0.84	4	27
Permethrin		1.4	7	380
Propyzamide		1.7	8	450
Simazine		0.60	3	58
Trifluralin		1.5	8	910
Vinclozolin		0.38	2	39,400

*Oxydemeton-methyl cannot be analyzed as part of this multi-pesticide analysis since it requires a separate analysis. Therefore, separate samples will be collected the last two weeks of this sampling period and analyzed for oxydemeton-methyl using a separate single-pesticide analytical method.

Table 2. Group 2—List of Candidate Compounds for Multi-residue Air Sampling Scheme (analysis by liquid chromatography/mass spectroscopy at Battelle). Monitoring is planned for September 2000.

Pesticide (Active Ingredient)	Breakdown product	Target limit of quantitation (ng/m³)	Preliminary screening level (ng/m³)
Acephate		5	800
Acephate	Methamidophos*		160
Anilazine		5	1,300
Benomyl		5	1,700
	DDVP (from Naled)	5	20
Ethephon		5	59,000
Maneb		5	160
Methomyl		5	26,000
Oxamyl		5	660
Thiodicarb		5	370
Thiophanate-methyl			3,400

*Methamidophos is also a pesticide active ingredient that is applied in the Lompoc area.

Table 3. List of pesticides and breakdown products the TAG reprioritized in 1999-2000 for air monitoring in Lompoc. These were chosen from the pesticides for which at least 90 reported pounds were applied in the Lompoc area for 1996-1998. Each pesticide on the initial list was separately ranked for pounds applied, vapor pressure, and toxicity. The top 17 from each of the three categories were combined to make up the list below. Status on the TAG 1998 priority list and status of monitoring activities in Phases 1 and 2 are also shown.

Pesticide	Breakdown Product	TAG list in 1998? ¹	Monitored in Phase 1?	Candidate for Phase 2 monitoring?	Why not a candidate for Phase 2?
<i>Acephate</i> ²		Yes	No	Yes	
Acephate	<i>Methamidophos</i>	No	No	Yes	
<i>Anilazine</i>		No	No	Yes	
<i>Benomyl</i>		Yes	No	Yes	
Benomyl	Methyl 2-benzimidazole carbamate (MBC) ³	No	No	No	Single method
Chlorothalonil ⁴		Yes	Yes	Yes	
Chlorpyrifos		Yes	Yes	Yes	
Chlorpyrifos	Oxygen analog	No	Yes	Yes	
Chlorthal-dimethyl		Yes	No	Yes	
Chlorthal-dimethyl	Monomethyl and tetrachloroterephthalic acid (TPA, MTP)	No	No	No	Single method
Cycloate		No	Yes	Yes	
Diazinon		Yes	Yes	Yes	
Diazinon	Oxygen analog	No	Yes	Yes	
Dicloran		No	No	Yes	
Dicofol		No	No	Yes	
Dimethoate		Yes	Yes	Yes	
Dimethoate	Oxygen analog	No	No	Yes	
Disulfoton		Yes	Yes	No	Single method
Disulfoton	Oxygen analog		No	No	Single method
EPTC		No	No	Yes	
Ethalfuralin		No	No	Yes	

¹ Alachlor, chloropicrin and fenamiphos were listed as priority pesticides by the TAG in 1998, but are not included in this list the TAG reprioritized. Chloropicrin, along with methyl bromide and MITC, has been included as a compound for monitoring in the fumigant and sampling plan. Alachlor and fenamiphos were not included in this reprioritized list because they no longer were among the top 17 chemicals when ranked by use, toxicity or vapor pressure (volatility).

² Battelle will attempt methods development for compounds shown in italics in this Phase 2 monitoring.

³ Compounds shown in bold were not included in the list of prioritized compounds for methods development.

⁴ UCD has developed methods for compounds shown in regular type in this Phase 2 monitoring.

<u>Ethephon</u>		No	No	Yes	
Fonofos		Yes	Yes	Yes	
Fonofos	Oxygen analog		No	Yes	
Fosetyl-Al		Yes	No	No	Difficult method, low toxicity
Glyphosate		No	No	No	Single method, low toxicity
Iprodione		Yes	No	Yes	
Malathion		No	No	Yes	
Malathion	Oxygen analog	No	No	Yes	
Mancozeb		Yes	No	No	Difficult method
Mancozeb	Ethylene thiourea	Yes	No	No	Difficult method
<i>Maneb</i>		Yes	No	Yes	
Maneb	Ethylene thiourea	Yes	No	No	Difficult method
Mefenoxam		No	No	Yes	
Metam sodium	MITC	Yes	Yes	Yes/Fumigant sampling	
Methyl bromide		Yes	Yes/Analysis by UN Reno	Yes/Fumigant sampling	
<i>Methomyl</i>		Yes	No	Yes	
Metolachlor		No	No	Yes	
Naled		No	No	Yes	
Naled	<i>DDVP (dichlorvos)</i>	No	No	Yes	
<i>Oxamyl</i>		No	No	Yes	
Oxydemeton-methyl		Yes	Yes	Yes	
PCNB		No	No	Yes	
Permethrin		Yes	Yes	Yes	
Propyzamide		Yes	No	Yes	
Simazine		No	No	Yes	
Simazine	Deethyl simazine, diaminochlorotriazine	No	No	No	Single method
Sulfur		Yes	No	No	Single method, low toxicity
Sulfuryl fluoride		No	No	No	Single method, study design does not include its residential structural uses

<i>Thiodicarb</i>		No	No	Yes	
<i>Thiophanate-methyl</i>		No	No	Yes	
Thiophanate-methyl	Methyl 2-benzimidazole carbamate (MBC)	No	No	No	Single method
Trifluralin		No	No	Yes	
Vinclozolin		No	No	Yes	

**Lompoc Pesticide Air Monitoring
Multiple-Pesticide Sampling and Analysis Plan**

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1. INTRODUCTION

1.1 Background

In 1997, the Department of Pesticide Regulation (DPR) formed the Lompoc Interagency Work Group (LIWG) to help investigate Lompoc residents' concerns (first voiced in 1992) about potential pesticide exposure from drift of pesticides during and following agricultural applications. To evaluate these concerns, information on the levels and amount of pesticides to which people may be exposed is required.

The LIWG is composed of staff from federal, state, county, and city agencies as well as community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air monitoring program, and to consider potential exposures from other environmental factors, such as crystalline silica and radon. The pesticide exposure subgroup (now called the Technical Advisory Group) developed a work plan that recommended comprehensive air monitoring in Lompoc during various seasons to determine whether, and in what amounts, pesticides occur in air in residential areas within the city of Lompoc. This exposure subgroup prioritized 46 pesticides based on their toxicity, amount used, and volatility (Appendix A).

The Technical Advisory Group (TAG) recommended a comprehensive monitoring program to span peak use periods for the top 23 chemicals in a two-phase program. The TAG did not recommend monitoring for the remaining 23 pesticides from the original list of 46, realizing fiscal resources were limited. The first phase of monitoring was recommended for the summer of 1998 (if only partial funding was available), and the second phase for early summer of 1999 (Appendix A). The monitoring recommendation was designed to measure maximum daily pesticide concentrations in air that could be compared to human health endpoints. The LIWG accepted the TAG recommendations and forwarded them to DPR in April 1998.

In August 1998, the Legislature passed Senate Bill 661, which provided funding to DPR to conduct the first phase of pesticide air monitoring. The first phase of monitoring was completed in September 1998 (results are summarized in Section 4.2). In May 1999, DPR received a grant from the U.S. Environmental Protection Agency (U.S. EPA) to monitor pesticide applications in the Lompoc area during fall and winter months. This monitoring began in January 2000 (see Section 4.3). The Governor's 1999 - 2000 budget allocated \$345,000 to DPR for monitoring pesticide air concentrations in the spring, summer, and fall 2000 in Lompoc. This document describes the monitoring planned for pesticides (other than fumigants) applied during the months of late May through early August and September 2000 using multiple-pesticide analysis of single samples.

The list of pesticides, although based partially on the list the TAG prioritized in 1998 (see Appendix A), is based on the TAG's more recent ranking of compounds in three categories using the most current information: (1) toxicity, (2) vapor pressure (volatility), and (3) use. The top 17 chemicals from each of these rankings then formed a group of

compounds that the TAG further reviewed. Finally, based on availability of analytical methods, DPR, in consultation with the TAG, created a candidate list of up to 39 compounds (32 pesticides and 7 breakdown products) for monitoring in this plan.

1.2 Pesticide Air Monitoring Objective

The objective of this study is to measure ambient concentrations in the air of as many of the pesticides as possible (based on their vapor pressure [volatility], toxicity and use) in the Lompoc area that are used during late May through early August and September 2000 for as long as possible, given analytical and funding constraints. DPR will compare these measured ambient air concentrations to human health screening levels (acute and subchronic) to determine what, if any, action to take. To evaluate chronic exposures, DPR plans to extrapolate from the several weeks of monitoring data collected in this study to estimate the annual average concentration that can be compared to chronic screening levels.

2. Data Quality Objectives for Pesticide Monitoring

2.1 Problem Description

Lompoc residents have voiced concerns about pesticide use as it relates to community health. An evaluation of available health-related data, including hospital discharges and cancer incidence, suggests that certain respiratory illnesses, such as asthma, bronchitis, and lung and bronchus cancers, occur in Lompoc at higher rates than in other comparison areas. To aid in the evaluation of the effect of pesticides on residents in Lompoc we first need to determine whether, and in what amounts, pesticides occur in ambient air within the city of Lompoc. Since the term pesticide constitutes a large number of chemicals, the measurement of air concentrations in Phase Two will be conducted in two parts. In this part of Phase Two, as described in this sampling and analysis plan, air measurements will be made for as many of the pesticides whose use, based on historical pesticide use reports (1996-1998), is expected to be highest in the spring, summer, or fall. (A separate sampling and analysis plan addresses Phase Two's other set of air measurements: monitoring air for fumigants, a subset of pesticides. To view this plan, visit DPR's home page at www.cdpr.ca.gov, click on Programs and Services, then click on the Lompoc Project.)

Since few methods exist (Majewski *et al.*, 1998; Foreman *et al.*, 1997; and see DPR's Phase One monitoring in Section 4.2) at this time for air monitoring where single samples can be collected and analyzed for multiple pesticides, methods development work was required to best use available resources to monitor as many pesticides of potential concern as possible. As part of the work the TAG conducted during the last year, it reviewed the pesticides used in Lompoc, developed a ranking scheme based on use, toxicity, and vapor pressure (volatility) to prioritize chemicals for which to request methods. DPR identified two potential laboratories to develop methods for and conduct multi-pesticide analysis of single samples during this last year.

Although the TAG originally recommended 23 pesticides, the TAG has since revised its recommendation to up to 32 candidate pesticides and 7 breakdown products, in addition to the four fumigants. Recently, DPR received the most recent pesticide use reporting data available (1998) for the Lompoc area. DPR, in consultation with the TAG, reviewed the list of chemicals to monitor and re-prioritized them based on this new use data, their physical and chemical characteristics (such as vapor pressure or volatility), toxicity including carcinogenicity, and availability of analytical methods. DPR's previous review was based on 1995 pesticide-use data; however, data for 1998 show seven new chemicals with more than 100 pounds used (Table 1). Use has more than doubled for another 11 chemicals (Table 1).

Specifically, the TAG reviewed the list of 127 pesticides that were used in Lompoc during 1996-1998 (Table 2), ranked them based on equal weighting of the most current use, toxicity, and vapor pressure information, selected the top 17 from each of these three lists, combined them and removed repeaters to produce a list of active ingredients and additional breakdown products (Table 3). Then DPR submitted this list to at least 12 analytical laboratories to determine their interest and ability to develop methods and analyze air samples for multiple pesticides, and selected two laboratories out of the three that replied to develop two methods for a candidate list of up to 32 pesticides and 7 breakdown products (Tables 4-5). See Appendix B for details about how the TAG selected compounds for the candidate list.

The TAG now recommends that the project sample as many of the 32 pesticides and 7 breakdown products as methods development allow, in ambient air for samples 24-hour in duration 4 days/week for several weeks at 4 sites during months of expected peak use for these pesticides. Recent use reporting information also shows that these pesticides are historically applied mainly in the spring, summer, and fall; therefore, DPR plans to monitor some pesticides from late May into early August and additional pesticides will be monitored in September 2000 (Tables 6-7).

Ambient¹ (i.e., surrounding outdoor) air concentrations of pesticides will be measured within the city of Lompoc and compared with their respective final (acute, subchronic and chronic) health screening levels². The U.S. EPA or California's Office of Environmental Health Hazard Assessment typically generates enforceable human health standards. Human health standards for ambient air have not been developed for these pesticides. The TAG has developed preliminary screening levels (see Appendix C) to ensure that the analytical methods' limits of detection are sufficient to allow assessment of risks from ambient exposure. Analytical methods used in this plan have been developed to detect concentrations that are well below these preliminary screening levels.

¹The TAG considers community outdoor air monitoring the most effective way to quantify the town's exposure to pesticides. Other types of monitoring, such as indoor air, partitioning dust/air, partitioning fog/air, and targeted monitoring near field applications, were all considered. However, these other types of monitoring are related to more specific exposures. If warranted, based on results from this sampling and analysis, other types of monitoring could be conducted at a later date.

² Acute exposure is an exposure for a short time, usually 24 hours or less. Subchronic exposure is an exposure for an intermediate period of time, generally one to three months. Chronic exposure is an exposure for extended periods of time, usually for a significant portion of a lifetime (Hodgson *et al.*, 1998).

These preliminary screening levels were generated using generally conservative assumptions to ensure that the analytical method detection limits will be lower than the final health screening levels.³ A subcommittee of the TAG will assist DPR in developing final health screening levels. See Appendix C for a brief description of this process. These levels will address acute and subchronic scenarios. The preliminary screening levels and the final health screening levels are not equivalent to legal human health standards and cannot be interpreted as such. However, DPR will use these to evaluate the potential health implications of the measured air levels.

The U.S. EPA is currently developing methods to address the risks from exposure to multiple chemicals. These and/or other methods will be used in an effort to evaluate multiple pesticide exposure, in addition to the pesticide-by-pesticide evaluation. This method(s) will include some sort of summation of risks across chemicals. For example, cancer risks may be summed and noncancer risks may be summed using a hazard index approach.

Identify Primary Decision-Maker - As the lead agency for the registration and use of pesticides in California, DPR is the primary decision-maker for this project.

Identify the Members of the Planning Team - DPR formed the LIWG to help investigate Lompoc residents' concerns. The LIWG is composed of staff from federal, state, and county agencies as well as staff from the city of Lompoc and community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to develop a pesticide air monitoring strategy, and to consider potential exposures from other environmental factors, such as crystalline silica and radon. The pesticide exposure subgroup (now called the TAG) assists in the planning, implementation, and evaluation of pesticide air monitoring in Lompoc. Members of the TAG are listed in Appendix D.

Specify Available Resources and Relevant Deadlines - This project is being conducted in phases due to complexity and funding constraints. This phase of the project focuses on monitoring for pesticides used in the Lompoc area in the spring, summer, and fall. DPR will provide personnel and resources for project supervision, administration, data compilation and analysis, and report preparation. The Governor's budget for 1999-2000 allocated \$345,000 to DPR that it would use to contract for sampling, analytical, meteorological, and quality assurance services. See Appendix E for the field sampling and laboratory analysis contracts. Members of the TAG provide in-kind contributions, such as project planning and supervision, compilation of pesticide use data, compilation of meteorological data, evaluation of data, and report preparation and review. Field sampling and laboratory analysis for this part will occur during the spring, summer, and fall of 2000.

³ The lowest preliminary screening level is 20 ng/m³ (Appendix C); Phase One maximum air concentrations of quantifiable samples range from 5.3 to 760 ng/m³ (see Section 2.7). UCD has predicted estimated quantitation limits (EQL) of 3 – 6 ng/m³ for organophosphates and 6 – 9 ng/m³ for compounds that require a mass selective detector for detection (Appendix I). Battelle has a predicted EQL of 5 ng/m³ (Appendix L).

2.2 Decision and Actions

Identify the Principal Study Questions - Do ambient air concentrations of these pesticides used in the Lompoc valley exceed the final (acute, subchronic or chronic) screening levels? DPR will monitor pesticides in two groups during their months of historical peak use. In late May, June, July, and early August, DPR will monitor as many of the 23 candidate pesticides and 5 breakdown products as possible from this first group whose expected high use period occurs during these months. UC Davis (UCD) will analyze each sample that DPR collects for these pesticides using gas chromatography (GC) as the analytical method. In September, during their expected period of high use, DPR will collect the second group of pesticides (and one breakdown product) that will be analyzed using liquid chromatography/mass spectroscopy (LC/MS) by Battelle. (See Section 2.1 for discussion of pesticide selection.)

Define Alternative Actions-

- (a) No action is taken (Table 8).
- (b) A more refined analysis is undertaken (Table 8).
- (c) Regulatory action is taken to reduce pesticide air concentrations (Table 8).

Combine the Principal Study Question and Alternative Actions into a Decision Statement -Determine if pesticide air concentrations are above final screening levels and if they are, determine if regulatory actions are required to mitigate them.

2.3 Inputs to the Decision

Identify the Information Required to Resolve the Decision Statement - There are two primary inputs required to resolve the decision statement, namely, air concentrations of pesticides in Lompoc and preliminary and final health screening levels for those pesticides. Air concentrations of pesticides in the Lompoc area will be measured directly in this study to generate the data needed to compare with the final screening levels. The TAG has already proposed preliminary screening levels. Toxicologists from DPR and the TAG will develop final health screening levels for each pesticide to be monitored. Other information may be useful and/or essential for interpreting pesticide air concentrations, such as meteorological data, and pesticide use records. While there is likely to be pesticide exposure from routes other than air (e.g., through ingestion of food, water or dust-borne residues that might result from pesticide use, or through dermal absorption), inhalation is of primary concern due to volatility or drift during application of these pesticides and documented respiratory illnesses in Lompoc.

Determine the Sources for Each Item of Information - Information on pesticide air concentrations will be obtained by direct measurement during late May through early August and September 2000. Pesticide use records from this period indicate a high use of these pesticides during spring, summer, and fall months (Table 7). Monitoring stations will be established in Lompoc to measure pesticide air concentrations during seasons of expected highest use, based on use in the past, for these pesticides. Monitoring will not be tied to specific applications; however, information on pesticide use during this season

will be obtained from pesticide use reports submitted by pesticide users to the Santa Barbara County Agricultural Commissioner's Office. The Santa Barbara County Agricultural Commissioner's Office will coordinate with monitoring personnel to provide use information in a timely manner. The Santa Barbara County Air Pollution Control District will measure meteorological conditions at its existing station in Lompoc. In addition, a MetOne station will be established in the agricultural area west of Lompoc and operated by staff from the DPR.

Confirm that the Appropriate Measurement Methods Exist to Provide the Necessary Data

-The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute (L/min) through a solid sorbent material onto which the pesticide is adsorbed (Keith, 1988). In addition, lower flow rates (< 1 L/min) have been used to trap pesticides and prevent breakthrough on sorbent media during air sampling (Ross *et al.*, 1996; Kollman, 1995). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel, 1995; Keith, 1988; Baker *et al.*, 1996). Chemical extraction methods for removing pesticides from sorbent media and analyzing with a gas chromatograph equipped with a detector or analyzing with liquid chromatography/mass spectroscopy provide quantitation of air concentrations below the preliminary and final screening levels and associated decision rules (Tables 9-11).

2.4 Study Design

Specify the Characteristics that Define the Population of Interest - The population of interest is the pesticides used in the Lompoc area. Based on pesticide use reports between 1996 and 1998, 127 pesticides were used in the Lompoc area. DPR, in consultation with the TAG, has reviewed these pesticides and ranked them based on five criteria: amount used in the Lompoc area, vapor pressure (volatility), toxicity, sufficient toxicological information to determine a target detection limit, and validated monitoring methods that achieve the target detection limit. This ranking provided the basis the TAG used to prioritize which pesticides to monitor in this plan (see Appendix B). Months of expected highest use for these chemicals include spring, summer, and fall. DPR plans to monitor as many of these high priority pesticides as possible.

Table 4 contains the first of two lists of candidate compounds whose physicochemical properties may be compatible with a single sample multiresidue air sampling/analysis scheme using XAD-4 resin as a trapping medium and analyzed by gas chromatography (Table 12). Due to limited laboratory resources, the maximum number of compounds that could be analyzed this year by this method will be confined to those listed in Table 4. The final list of compounds to be analyzed during this sampling and analysis plan will be determined after the method development phase is completed. The final list will be as many of the compounds as possible, and will be determined by the University of California Davis' Trace Analytical Laboratory and DPR personnel. The samples analyzed by UCD will be collected over a consecutive 10-week period, during the months of late May through early August.

Table 5 contains the second list of candidate compounds whose physicochemical properties may be compatible with a single sample multiresidue air sampling/analysis scheme using XAD-4 resin as a trapping medium, and liquid chromatography/mass spectroscopy analysis (Table 12). Before the end of the method development phase, Battelle Atmospheric Science and Applied Technology Department (Battelle) Laboratory will contact DPR and mutually establish the final target analyte list. Those samples for Battelle will be collected in September.

Define the Spatial Boundary of the Decision Statement – The spatial boundary of the decision statement is the outdoor air within the Lompoc city limit. The city of Lompoc, 11.3 square miles in area, is located in a coastal valley of Santa Barbara County, California, approximately eight miles east of the coastline (Figure 1). The valley is oriented roughly northwest to southeast. Between the city and the ocean lies an agricultural region predominantly devoted to vegetable and flower production. Predominant wind patterns during spring, summer, and fall months tend to be from the northwest, moving across the agricultural region and into the city of Lompoc (Johnson, 1998; Figures 2 and 3).

For the purposes of this study, the boundary of the pesticide-use area is 38.8 square miles (Figure 3) and consists of the Township-Range sections listed in Tables 13-14. This list of sections was previously accepted by the LIWG as reasonable for defining the area of pesticide use that could potentially affect air in the city of Lompoc.

Air monitoring will be conducted at four sites located inside the city limits of Lompoc. Three of the four air sampling sites were selected to be representative of areas where the highest pesticide concentrations are hypothesized, based on proximity to pesticide application sites and predominant wind patterns during that time of year. The fourth site, near the center of Lompoc, was selected to be representative of pesticide concentrations that might be found closer to the center of the city. DPR also used these as the monitoring sites in its Phase One pesticide air sampling and in its Phase Two fumigant sampling and analysis. Although a fifth site, located in the northeast region of Lompoc to capture applications that might occur in the smaller agricultural areas to the north and east of the city, was used in the fumigant sampling and analysis plan, the TAG decided not to include it in this plan because past pesticide use has not been demonstrated to be high and the prevailing winds would move the applications in this area away from Lompoc (Figure 2).

Define the Temporal Boundary of the Decision Statement – In this project we will monitor air concentrations of as many of the candidate compounds as possible during the spring, summer, and fall (late May through early August, and September 2000), a period when these pesticides historically have been used in the highest amounts (Table 7; DPR 1996, 1997a, and 1998) and a time of year when air inversions in the Lompoc valley are anticipated.

For each pesticide being evaluated, concentrations are measured in the ambient community air. The monitoring will be done during the expected season of peak use.

The expected season of peak use is determined by reviewing pesticide use reports from 1996 – 1998 (see Tables 6-7). For ambient air measurements of Group 1 pesticides, DPR will monitor for 10 consecutive weeks at 4 sites, collecting 4 24-hour samples/week. This monitoring schedule will be followed in late May, June, July, and early August when DPR will monitor for the first grouping of chemicals (Table 4) during their expected peak use season. Oxydemeton-methyl samples cannot be analyzed as part of this multi-pesticide analysis since oxydemeton-methyl requires a separate analysis. Therefore, separate samples will be collected the last two weeks of this sampling period and analyzed only for oxydemeton-methyl. The County Agricultural Commissioner will be contacted to confirm use during that time. Since this single pesticide analytical method requires additional funding, limited oxydemeton-methyl sampling will be conducted as follows: samples 24-hours in duration will be collected 4 days per week for 2 weeks at 2 sites.

In September, DPR plans to monitor as many of these compounds for which methods have been developed (Table 5) during their expected high use season for at least 3 consecutive weeks, collecting 4 24-hour samples/week at 4 sites.

These lists of chemicals (Tables 4-5) do not include one chemical included in Phase One [disulfoton, an organophosphate that would be analyzed by gas chromatography as part of Group 1] because additional preparative steps are required before analysis by gas chromatography. If every sample in Group 1 (Table 4) were analyzed for this chemical, additional costs would be incurred which would then reduce the number of samples for the other pesticides analyzed by gas chromatography.

Air sampling will be conducted for 24 hours per sample.

Scale of Decision Making - Decisions will be based on air concentrations measured at the monitoring sites established in the city of Lompoc.

Identify Practical Constraints on Data Collection - There are several constraints on data collection:

1. The time of monitoring is constrained to the peak use seasons (spring, summer, and fall months), namely late May through early August, and September 2000, preferably for each pesticide monitored. Sampling is to be conducted during these months when historically these pesticides have the highest use (Table 7). However, each pesticide of interest does not have the same peak use season.

Mitigation of Constraint: DPR plans to monitor pesticides in two time periods. One time period will occur during late May through early August for those pesticides whose expected peak use occurs then, the other time period will occur during September for those pesticides whose expected peak use occurs in these months.

2. Sampling during spring, summer and fall periods does not necessarily ensure that maximum concentrations will be measured since air concentrations depend on factors other than use, including meteorological conditions, and location of applications relative

to air samplers.

Mitigation of constraint: We are not able to mitigate.

3. Siting criteria for air sampler locations might prevent monitoring at locations of actual maximal concentration. The location of monitoring is constrained to the city of Lompoc and places within that which meet the U.S. EPA siting criteria (Appendix F). Sites not meeting these criteria may have higher concentrations.

Mitigation of constraint: None.

4. Due to monetary constraints, monitoring cannot be conducted on each day of the high use season, therefore days not monitored might have higher or lower concentrations.

Mitigation of constraint: In the final report, DPR will compare the monitoring results at the different sites with daily pesticide use and meteorology data to assess the representativeness of the data.

5. Concentrations will be measured during 24-hour periods. Some chemicals can cause effects during shorter duration exposures.

Mitigation of constraint: This is a standard toxicological practice.

6. Due to monetary constraints, this study will only provide information on pesticide active ingredients except in the case of acephate, chlorpyrifos, diazinon, dimethoate, fonofos, malathion, and naled where the active ingredient and only the primary breakdown product will be analyzed (see Section 6.1). Also, data will not be gathered for inert ingredients, adjuvants, industrial chemicals, or other pesticide product components that could potentially affect human health.

Mitigation of this constraint: There is no mitigation for this constraint. At this time there are no funds for monitoring of additional chemicals.

7. Some pesticides may have agricultural and non-agricultural uses in the area (e.g., home uses). There will be insufficient information to determine the relative contributions of each source to the overall air concentrations measured.

Mitigation of constraint: We are not able to mitigate.

8. This study will only estimate inhalation exposure. Potential exposure to pesticides by ingestion, dermal absorption, or other potential routes will not be measured.

Mitigation of constraint: There is no mitigation planned for this constraint because for pesticides, the major route of exposure is expected to be through inhalation.

9. Some concentrations may be too low to quantify given the current state of our

technology for chemical analysis.

Mitigation of constraint: Data below the limit of quantitation will be set equal to one half the limit of quantitation for all exposure calculations.

10. Three monitoring sites are located on the western edge of Lompoc in an effort to measure maximum concentrations. This placement does not guarantee that higher concentrations will not occur at other locations. Based on our knowledge of wind patterns and the location of agriculture relative to Lompoc, this was deemed the logical place to focus our sampling efforts.

Mitigation of constraint: We are not able to mitigate.

11. Due to monetary constraints, not all pesticides used in the Lompoc Valley can be monitored.

Mitigation of constraint: The TAG identified pesticides that DPR will monitor in air to collect data to use in evaluating their potential to be toxic air contaminants. The TAG ranked these pesticides based on toxicological properties, physical and chemical properties, and the amounts used in Lompoc. The TAG used this ranking as the basis for prioritizing the pesticides to monitor in this plan. Then the final target compounds were selected based on available analytical methods.

12. Insufficient toxicological information exists to determine the possible health hazard from exposure to multiple chemicals.

Mitigation of constraint: As part of the implementation of the Food Quality Protection Act, the U.S. EPA is developing methods to assess the health risk of exposure to multiple pesticides that share a common mechanism of toxicity. As these methods are developed and validated, they will be used to evaluate this question.

13. The multiple-pesticide analysis of samples may tentatively identify compounds that are not on the candidate pesticide lists (Tables 4-5).

Mitigation of constraint: None. It is beyond the scope of this project to definitively identify tentatively identified compounds that may be detected but are not listed in these tables.

14. Following applications, pesticides (other than those applied as dusts) move away from the target field by drift and post-application volatilization in two forms: gaseous and adsorbed onto airborne particulates. Although the sample analysis does not account for all the particulate, we believe that the fraction we may be missing is a small percentage. Due to monetary constraints, it is beyond the scope of this study to collect and analyze such samples.

Mitigation of constraint: Samples for particulates may be collected to estimate the

missing fraction, should funds become available.

2.5 Decision Rule

Specify the Statistical Parameter that Characterizes the Population – For evaluating acute exposure to ambient air levels of individual pesticides monitored in this study, the parameter of interest will be the maximum 24-hour air concentration at any site during each monitoring period. In addition, DPR will look at patterns in the 24-hour measurements.

For evaluating subchronic exposure to ambient air levels of individual pesticides monitored in this study, the parameter of interest will be the maximum average of the highest 8 days at any site. This will be referred to as the maximum 8-day average⁴. DPR may also examine other combinations.

For evaluating chronic exposure to ambient air levels of individual pesticides monitored in this study, the parameter of interest will be the annual average. The estimation of annual average concentration is explained in Section 8.1.

Specify the Action Level for the Study – For the purposes of this study, the action levels will be the final health screening levels. The TAG has developed preliminary screening levels (Appendix B) to ensure that the limits of detection are adequate. DPR's toxicologists, in conjunction with toxicologists from the TAG, will develop final health screening levels for acute, subchronic and chronic exposures (Appendix B).

Develop a Decision Rule – Acute exposure: If the maximum 24-hour air concentration is significantly below the final acute health screening level, no immediate action will be taken. If the maximum 24-hour air concentration is below the screening level, but not significantly below it, DPR may still consider further analysis (e.g., further monitoring, and/or a more detailed analysis of the health effects data). However, if the maximum 24-hour air concentration is greater than the final acute health screening level, then DPR will respond immediately with development of a plan for further analysis and/or interim regulatory action. Regulatory actions could consist of one or more of the following: permit conditions for restricted materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study.

Subchronic exposure: If the maximum 8-day average air concentration is significantly below the screening level, no immediate action will be taken. If the maximum 8-day average air concentration is below the screening level, but not significantly below it, DPR may consider further analysis (e.g., further monitoring, and/or a detailed analysis of the health effects data). If the maximum 8-day average air concentration is greater than the final subchronic health screening level, then DPR will respond immediately with the development of a plan for further analysis and/or interim regulatory action. Regulatory actions could consist of one or more of the following: permit conditions for restricted

⁴ Note: Eight days represents two weeks of sampling (i.e., DPR collects 4 24-hour samples per week).

materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study.

Chronic exposure: If the estimated annual average air concentration is below the final chronic health screening level, no immediate action will be taken. If the estimated annual average air concentration is above the screening level, DPR will conduct further analysis (e.g., further monitoring, and/or a detailed analysis of the health effects data).

2.6 Decision Errors and the Null Hypothesis

Define Both Types of Decision Errors and Establish the True State of Nature for Each Decision Error – There are two decision errors, i) deciding that the maximum air concentration exceeds the final health screening level when it does not, and ii) deciding that the maximum air concentration does not exceed the final health screening level when it does.

The true state of nature for decision error (i) is that the maximum 24-hour (or the maximum 8-day average, or annual average) air concentration does not exceed the final health screening level.

The true state of nature for decision error (ii) is that the maximum 24-hour (or the maximum 8-day average, or annual average) air concentration exceeds the final health screening level.

Specify and Evaluate the Potential Consequences of Each Decision Error - (i) If the maximum 24-hour (or the maximum 8-day average, or annual average) air concentration does not exceed the final screening level, but inadequate or incorrect data indicate that it does, DPR would mitigate the exposure without sufficient cause. This has implications for pest management, alternative pesticides, crop yields, and costs to growers and consumers. (ii) If the maximum 24-hour (or the maximum 8-day average, or annual average) air concentration does exceed the final health screening level, but inadequate or incorrect data indicate that it does not, a potential public health hazard might not be mitigated.

Establish Which Decision Error has More Severe Consequences Near the Action Level - Decision error (ii) has the more severe consequences because an unmitigated health hazard outweighs the consequences of economic costs.

Define the Null Hypothesis (Baseline Condition) and the Alternative – Acute exposure: The baseline condition or null hypothesis is that the maximum 24-hour air concentration exceeds the final acute health screening level. The alternative hypothesis is that the maximum 24-hour air concentration is below the final acute health screening level. Subchronic exposure: The baseline condition or null hypothesis is that the maximum 8-day average air concentration exceeds the final subchronic health screening level. The alternative hypothesis is that the maximum 8-day average air concentration is below the final subchronic health screening level.

Chronic exposure: The baseline condition or null hypothesis is that the annual average

air concentration exceeds the final chronic health screening level. The alternative hypothesis is that the annual average air concentration is below the final chronic health screening level.

Specify a Range of Possible Values of the Parameter of Interest Where the Consequences of Decision are Relatively Minor (Gray Area) – The screening levels all incorporate conservative uncertainty factors. Exceeding a final health screening level, therefore, does not mean that a health impact will in fact occur. It implies that the margin of safety built into the level is being eroded. The greater the exceedance, the closer the exposure will be to an adverse effect level. This occurs on a continuum, rather than at a specific point. There is a “gray” area above the screening level, where there are not expected to be adverse health consequences of erroneously rejecting the null hypothesis. For chlorpyrifos, the gray area for acute effects is the region between the acute screening level (1,600 ng/m³) and about 8,200 ng/m³. For subchronic effects, the gray area is the region between the subchronic screening level (1,600 ng/m³) and about 4,900 ng/m³ (Schreider, 2000).

Specify Tolerable Probability of Decision Errors

True value of parameter	Type of error	Tolerable probability of error
Below screening level	i) Conclude maximum concentration is above screening level.	30%
Gray area (just above screening level)	ii) Conclude maximum concentration is below screening level.	10%
Above the gray area	ii) Conclude maximum concentration is below screening level.	1%

2.7 Optimized Design for Obtaining Data

Review the Data Quality Objective Outputs and Existing Environmental Data - The TAG will review the data quality objectives (DQOs) and Multiple-Pesticide Sampling and Analysis Plan, in addition to the DQO outputs.

In Phase One monitoring, only chlorpyrifos had a substantial number of positive samples (29%). Chlorothalonil was detected in trace amounts (< 8 ng m⁻³) in 24 % of samples. Cycloate was found in seven samples; five were between 7.1 and 69.2 ng m⁻³, but the other two had 739 and 760 ng m⁻³.

Summary of Phase One Monitoring Data ^a

Pesticide	Number of positive samples	Number of quantifiable samples	Maximum	Mean ^b	Coefficient of Variation ^b
			----- ng/m ³ -----	-----	--- % ---
Chlorothalonil	28	0	< 8	-	-
Chlorpyrifos	34	34	83.1	5.91	177
Chlorpyrifos OA	4	4	8.5	-	-
Cycloate ^c	7	7	760	14.8	640
Diazinon ^c	3	3	18.2	-	-
Diazinon OA ^c	1	1	5.3	-	-
Dimethoate	0	0	< 1	-	-
Oxydemeton- methyl	0	0	< 1	-	-
Permethrin ^c	1	0	< 9	-	-

^a 119 total samples per chemical (5 sites x 20 days, including 4 days with co-located samplers at all sites, and one day with only 4 sites monitored).

^b Calculated using all samples; nondetects given value of ½ LOD.

^c Found only at NW and/or SW sites.

Alternative Data Collection Approaches – Two possible approaches to data collection are outlined below, with a minimum of one strength and one limitation expressed for each.

Ambient Air Monitoring Approach –

One approach would be to conduct ambient air monitoring within the city of Lompoc.

Air concentrations are considered an integral part of any study of the relationship between pesticide levels in air and community health effects. The strength of this approach is that air levels are measured, not estimated from a model. The limitation of this approach is that concentrations associated with all possible combinations of pesticide use and meteorological conditions cannot be monitored.

Application Site Monitoring -

Another alternative is to measure application site air concentrations and subsequently model the air concentrations projected for ambient air in the city of Lompoc. Application site monitoring would be used to back-calculate flux rates for each pesticide. This flux rate would then be incorporated into the model to then project ambient air concentrations within the city limits. The strength of this approach is that it would provide much needed information on various flux rates that might be expected from pesticide applications. The limitation of this approach is that it is more expensive than the other approaches. It also does not supply the desired information about measured air concentrations within the city limits. Air concentrations measured outside the city limits do not meet the stated goals and objectives of the plan nor does it conform to the desired study boundary conditions outlined above. We have selected the ambient air monitoring approach as the most cost effective approach that still meets our study objectives.

Develop General Data Collection Design Alternatives –

Simple Random Sampling -

For the present study, simple random sampling would involve choosing the sample locations by selecting points randomly in three spatial dimensions (i.e., latitude, longitude, and height), and choosing the sample starting times randomly within the study period.

Systematic Sampling -

Systematic sampling would involve choosing the sampling locations at evenly spaced distances in the three spatial dimensions, and choosing the sample times at evenly spaced intervals.

Stratified Random Sampling –

Stratified random sampling would divide the study area into distinct subareas with different, known probabilities of having the highest 24-hour concentration. Similarly, the study period would be divided into subperiods with different, known probabilities of having the highest 24-hour concentration. A predetermined proportion of the total samples would be randomly selected from each subarea/subperiod combination, with the proportion depending on the probability of highest concentrations in that combination.

Because it is desirable to maximize the probability of capturing peak concentrations, and because peaks are expected to be associated both spatially and temporally with pesticide applications, neither Simple Random Sampling nor Systematic Sampling would be very efficient. Stratified Random Sampling would be preferred, if the data existed to define the strata. However, existing monitoring data are not adequate to characterize statistically the spatial and temporal distribution of peak concentrations. Moreover, because of the practical constraints on location and scheduling of sampling events, none of the three design alternatives outlined can be implemented.

The proposed study design calls for 160 24-hour samples for Group 1 pesticides (4 sites times 1 sample/day times 4 days/week times 10 weeks) and 48 24-hour samples for Group 2 pesticides (4 sites times 1 sample/day times 4 days/week times 3 weeks).

The proposed study design most resembles systematic sampling, in that the monitoring sites and times were chosen to give reasonably even coverage, within practical constraints, of the area and seasons judged probable to have the highest concentrations.

Formulate the Mathematical Expressions Needed to Solve the Design Problem for the Data Collection Design – Because the study design is not statistically based, statistical methods for estimating precision or power must be considered as providing approximate guidelines only.

Chlorpyrifos was the most heavily applied nonfumigant among the pesticides monitored in Phase One (1998), and also had the greatest number of positive samples. The statistical calculations related to the design of the study have therefore been done using the Phase One chlorpyrifos data along with the preliminary subchronic screening level for chlorpyrifos.

In order to calculate the error probabilities of a statistical test, it is necessary to postulate a parent population and values of the population parameter of interest. The parent population in the present case is thought of as consisting of infinitely many sites, each sampled for an infinite number of days. Ambient air concentrations typically have lognormal distributions. In this case, it was assumed that both mean site concentrations and daily concentrations at each site are lognormally distributed. To test these assumptions, observations were simulated in a two-stage process. First, four site means were generated from a lognormal distribution with a mean of 6.08 ng m⁻³ and CV of 70% (the values estimated in Phase One). Then for each site, 40 “days” were generated from a lognormal distribution with mean equal to the site mean generated in the first stage and a CV of 165% (as estimated in Phase One). The overall mean, overall CV, site-mean CV, within-sites CV, maximum value and maximum 8-day average were very similar to those observed in Phase One (table below).

Comparison of two-stage simulation output with observed data for chlorpyrifos.

	Two-stage Simulation ^a	Observed in Phase One
Overall mean	6.18 ng m ⁻³	6.08 ng m ⁻³
Overall CV	180 %	180 %
Maximum 24-hr concentration	97 ng m ⁻³	83 ng m ⁻³
Maximum 8-day concentration	37 ng m ⁻³	31 ng m ⁻³
Site-mean CV	65 %	70 %
Within-sites CV	171 %	165 %

^a Mean values in 1000 simulations.

In the power calculations, both CVs were increased by 25%: to 88% for the site-mean CV and to 206% for the within-sites CV. This was done to allow for possible greater variability in the population than was captured in Phase One sampling.

The population parameters of interest are the maximum 24-hr concentration for acute exposure, and the maximum 8-day average for subchronic exposure. The maximum value in a lognormal distribution is undefined, being infinite. Therefore, the distributions under the null and alternate hypotheses were defined in terms of the population 99th percentile. In order to be able to specify distributions with certain 99th percentiles, a series of simulations was run to determine the relationship between overall site mean and the 99th percentiles of the maximum value and maximum 8-day average. Ten simulations were run as described above, using different values for the site mean and with the site-mean and within-sites CVs fixed at 88 and 206%, respectively. Between 10 and 350 ng m⁻³ (mean values), the relationship between site mean and the 99th percentile of the parameter of interest was found to be linear ($r^2 = 0.995$) for both acute and subchronic. The linear relationships were therefore used to choose site-mean values to achieve different target 99th percentiles in doing the power calculations.

The critical values for the hypothesis tests were found by simulating the distribution of the relevant maximum under the null hypothesis, i.e., with the 99th percentile equal to the screening level. The 10th percentile of the null distribution is the $\alpha = 0.10$ critical value, i.e., the null hypothesis will be rejected if the observed maximum is less than this value. For the maximum 24-hr concentration, the critical level is 100 ng m⁻³. For the maximum 8-day average, the critical level is 200 ng m⁻³. (It may seem anomalous that a lower value is required to reject the null hypothesis for acute exposure. A single value is much more variable than an average of several values, thus a lower value must be observed to conclude with the same confidence that the single value is below the screening level.)

Power of the statistical tests against alternate hypotheses were calculated by simulating 2,000 sets of 160 values using the two-stage process described previously. In each set, the relevant maximum was found, and the null hypothesis that the maximum is greater than the screening level was tested at the $\alpha = 0.10$ level. The power of the test is the proportion of the 2,000 sets in which the null hypothesis is rejected. The results are shown separately for the acute and subchronic hypothesis tests in the two tables below.

Error probabilities for the test of H_0 :
Maximum 24-hour concentration of chlorpyrifos $\geq 1,600$ ng m⁻³.

Type of Error	True Value of Parameter (99 th %ile ng m ⁻³)	Probability of Error
Null Hypothesis True		
Reject H_0 (conclude true maximum below screening level)	3,900	0.00
	3,000	0.01
	1,600	0.13
Null Hypothesis False		
Do not reject H_0 (conclude true maximum above screening level)	1,000	0.53
	750	0.26
	500	0.03

Error probabilities for the test of H_0 :
Maximum 8-day concentration of chlorpyrifos $\geq 1,600 \text{ ng m}^{-3}$.

Type of Error	True Value of Parameter (99 th %ile $\mu\text{g m}^{-3}$)	Probability of Error
Null Hypothesis True		
Reject H_0	4,900	0.00
(conclude true	3,000	0.01
maximum below	2,100	0.02
screening level)	1,600	0.13
Null Hypothesis False		
Do not reject H_0	1,000	0.60
(conclude true maximum	770	0.36
above screening level)	400	0.07
	240	0.01

The estimation of annual average concentration (see Section 8.1) from 3 to 10 weeks of monitoring data will be very approximate, at best. The sampling characteristics of the estimator are unknown. Therefore, no calculations of error probabilities for the chronic exposure test can be done.

Select the Optimal Samples Size that Satisfied the DQOs – The power calculations indicate that the planned 40 days at each of four sites should be adequate to achieve close to the desired error probabilities. Both tests, but especially the test of acute exposure, are very conservative, in that it is difficult to reject the null hypothesis. Note that a true maximum 24-hr concentration of 500 ng m^{-3} , with 0.03 probability of (incorrectly) failing to reject the null hypothesis, is associated with an overall mean of 7 ng m^{-3} , approximately that observed in Phase One. A true maximum 8-day concentration of 240 ng m^{-3} is associated with the overall mean of 7 ng m^{-3} . For both tests, the probabilities of incorrectly rejecting the null hypothesis (i.e., incorrectly concluding that the maximum is below the screening level) are very low.

Document the Operational Details and Theoretical Assumptions of the Selected Design in the Sampling and Analysis Plan – Three sampling sites will be established on the west side of Lompoc, closest to the agricultural area and where the highest concentrations are expected. One site will be located in the northwest corner of Lompoc, one on the center-west side, and one in the southwest corner (Figure 3). An additional site will be located near the central part of Lompoc, as recommended by the TAG during a conference call discussion on April 26, 2000.

Monitoring locations were selected to represent the portion of the city that would likely have the highest pesticide concentrations, given the location of applications and general wind patterns in the valley. Modeling potential pesticide concentrations in the city to

help locate air-sampling locations was not conducted. The possibility of conducting this type of modeling was discussed with technical staff from the Air Resources Board, U.S. EPA, and DPR at a meeting held on Oct. 5, 1999 in Sacramento. It was decided by meeting participants not to model air concentrations to assist with site selection due to: (1) the uncertainty and variability in model-input data, (2) the amount of time required to make multiple model runs of even a small fraction of the potential application and wind pattern combinations, and (3) the inability for modeled outputs to pinpoint the one site expected to have the peak concentration.

Monitoring will occur during a high use period as indicated by pesticide use reports. The number of applications that will occur during this period is unknown; some pesticides may not be applied at all.

3. SITE DESCRIPTION

3.1 Topography

The city of Lompoc is a small city located in a coastal valley of Santa Barbara County, California (Figure 1). The population has been estimated at 37,649 in a U.S. Census conducted in 1990. The city is located approximately seven to eight miles east of the coastline. The valley is oriented roughly northwest to southeast and the surrounding hills form a V shape fanning out towards the ocean. Hills to the east of Lompoc tend to stall air movement as it passes the city, while the air is funneled eastward through the Santa Ynez River basin. Vandenberg Air Force Base (a rocket launch facility) and agricultural fields dominate the area between Lompoc and the coast. Five major crops or crop groups are grown in this area: cole crops (broccoli, cabbage, and cauliflower), lettuce, dried beans, celery, and flowers.

3.2 Climate

A Pacific high-pressure area dominates the region in summer months. This high-pressure area tends to produce northwesterly winds in the Lompoc area (Figure 2). Aiding this tendency, the Central Valley of California heats up during the summer and creates a large pressure and temperature differential between inland and ocean surfaces. The air aloft from the Pacific high is generally warming and descending as it approaches the coastline near Vandenberg Air Force Base. Consequently, the cool moist marine area below tends to form a subsidence inversion accompanied by frequent fog or low cloudiness. The northwesterly winds exert pressure on the ocean surface that causes up welling of cool water. This cools the air near the surface and contributes to fog formation. During winter, the Pacific high weakens, the jet stream shifts southward, and heating of the Central Valley is weaker or absent. Winds tend to be more westerly and frontal systems move through the area, changing the wind direction more frequently than in summer months. This summary and a complete description of weather patterns for Lompoc are given in Johnson, 1998.

3.3 Pesticide Use

The information given in this section was extracted from DPR's pesticide use report database. A complete description of the pesticide use report database is given in DPR, 1995.

Between 1996 and 1998, approximately 127 pesticides have been used for agricultural production in the Lompoc area, with approximately 120,000 pounds used per year. Consistent with the crops and climate, insecticides and fungicides are the most heavily used pesticides in the Lompoc area (Table 2).

Because of their volatility, amount used in the Lompoc area, toxicity, sufficient toxicological information to determine a target detection limit, and validated monitoring methods that achieve the target detection limits (Tables 6, 9-12), DPR and the TAG identified these 33 pesticides and six breakdown products (Tables 4-5) as the focus of the monitoring described here.

The Township, Range, and sections, plus patterns of pesticide use summarized for 1996 through 1998 are displayed in Figure 4, and Tables 6, 7, 13, and 14. Table 15 lists the uses of these pesticides.

4. PREVIOUS INVESTIGATIONS

4.1 Study of Hospital Discharges

An analysis of hospital discharge data from 1991-1994 suggests that certain respiratory illnesses occur in Lompoc at higher rates than in other comparison areas. The State's Office of Environmental Health Hazard Assessment evaluated these data (Wisniewski *et al.*, 1998; Ames and Wisniewski, 1999). The evaluation indicated that the proportion of hospitalizations due to respiratory illnesses, in particular bronchitis and asthma, were elevated in Lompoc relative to the proportion of hospitalizations in the comparison areas, with some differences by age. The incidence of lung and bronchus cancers also was increased above the expected numbers based on regional rates. The purpose of the report was not to speculate on the cause of the illnesses; rather, it was to evaluate the incidence of specific illnesses.

4.2 Phase One of Pesticide Air Monitoring

The Phase One study was intended to test pesticide sampling and analysis methods and to determine if a subset of the total pesticides in use in the area could be measured in air (Okumura, 1999). With some exceptions, these goals were achieved. The study was most successful in developing and demonstrating the multiple-pesticide sampling and analysis method. This study provided the basis for the multiple-pesticide sampling and analysis approach this plan follows. Due to the limited nature of the Phase One sampling, these results are not appropriate for risk assessment.

Over 50 pesticides were used in or near Lompoc during the August-September 1998 monitoring period. Air monitoring was conducted for twelve pesticides with recorded use in those months in prior years. Of the 12, five were not applied during the 1998 monitoring period, and were not detected in air samples. The remaining seven were detected in air samples. Many of these detected concentrations were between the sample detection limit and quantitation limit meaning that the existence of the pesticide in a sample, while likely, was too low to be assigned a numerical value. For example, chlorpyrifos, the most frequently detected pesticide, was detected in 55 of 119 samples above the quantitation limit of 4 ng/m³, and in an additional 60 of 119 samples between the quantitation limit and the detection limit of 1 ng/m³. The maximum concentration of chlorpyrifos that was detected was 83 ng/m³.

Of the 12 pesticides that were monitored in Phase One, seven will be monitored in this sampling and analysis plan: chlorpyrifos and chlorpyrifos oxon, chlorothalonil, diazinon and diazinon oxon, dimethoate, fonofos, oxydemeton-methyl, and permethrin. DPR also plans to monitor cycloate that was detected in Phase One monitoring.

Chlorpyrifos results from Phase One are described above. In addition, chlorpyrifos oxon was detected in 4/119 samples above the quantitation limit of 5 ng/m³. The maximum concentration of chlorpyrifos oxon was 8.5 ng/m³. Chlorpyrifos oxon was not detected above the detection limit of 5 ng/m³ in 115/119 samples.

Chlorothalonil was detected in 28/119 samples between the quantitation limit of 8 ng/m³ and the detection limit of 2 ng/m³. Chlorothalonil was detected in 91/119 samples below the detection limit; no samples were detected above the quantitation limit.

Cycloate was not one of the 12 pesticides on the monitoring list, but was detected during laboratory screening. Concentrations of cycloate are considered to be estimates because of limited laboratory quality assurance. Cycloate was detected in 7/119 samples above the quantitation limit of 9 ng/m³. Its maximum concentration was 760 ng/m³. The rest of the samples were below the detection limit of 2 ng/m³.

Diazinon was detected in 3/119 samples. Its maximum concentration was 18 ng/m³. The remaining 116/119 samples were below the detection limit of 1 ng/m³. Diazinon oxon was detected in 1/119 samples above the quantitation limit of 5 ng/m³; its concentration was 5.3 ng/m³. Diazinon oxon was detected below the detection limit of 5 ng/m³ in 118/119 samples.

For chlorpyrifos and diazinon, while the analytical methodology gave an accurate estimate of the total concentration (parent plus oxygen analog, i.e., oxon), the sampling methodology gave an erroneously high proportion of the oxygen analogs and an erroneously low proportion of the parent compounds.

All 119 dimethoate samples were below the detection limit of 1 ng/m³.

Fonofos was not applied during the Phase one monitoring period, nor was it detected.

Oxydemeton-methyl was detected in 2/119 samples, but not quantified or confirmed. The detection limit was 1 ng/m³ and the quantitation limit was 5 ng/m³.

Permethrin was detected in 1/119 samples between the quantitation limit of 9 ng/m³ and the detection limit of 2 ng/m³. The rest of the samples were below the detection limit. The metal analyses were originally intended as surrogates for pesticides containing metals (aluminum in fosetyl-Al, and manganese in maneb and mancozeb). In retrospect, these analyses are not capable of discriminating between pesticide-applied sources and natural background sources, e.g., soils. Results should not be interpreted as indicative of the presence or absence of these metal-containing pesticides in air.

Silicon was tested for and found in Lompoc air during the monitoring period. Levels were found as high as 17 µg/m³, close to the highest level measured in California urban areas during recent years.

4.3 Phase Two of Pesticide Air Monitoring – Fumigant Sampling and Analysis

As stated previously, this ambient air monitoring project is being conducted in phases due to its complexity and funding constraints. This part of the project focuses on fumigants.

Fumigants are a unique class of pesticides. They are highly volatile, applied infrequently but at higher rates than other pesticides, and used to control a wide variety of pests and diseases. Since fumigants are applied before planting, many applications occur during the fall and winter. Because of their high volatility, high application rates, and season when most applications occur, fumigants are the focus of this part of the monitoring project.

This ambient air monitoring targets four fumigants: 1,3-dichloropropene (Telone), chloropicrin, metam sodium, and methyl bromide. Air sampling of each of these fumigants is coordinated with an application of the respective fumigant so that ambient air samples are collected during an application of a particular fumigant.

To date, DPR has monitored during four applications of metam sodium that occurred during January and February 2000. The Department of Health Services' laboratory has analyzed all the samples and processed results from all four applications. Further monitoring is on hold until sufficient resources for a second canister method are available, and the U.S. EPA reviews results from the first four applications. The Fumigant Sampling and Analysis final report will be available in 2001.

4.4 Air Concentrations of Pesticides Measured in California

The Air Resources Board, in consultation with DPR, conducts ambient monitoring for a variety of pesticides in accordance with the Toxics Air Contaminant (TAC) monitoring program. Monitoring for pesticides is conducted in counties with the highest use for a particular pesticide to be monitored and during the season of highest use. Information is available from air sampling conducted under the TAC program for ten of the pesticides to be monitored in Phase Two: benomyl, chlorothalonil, diazinon, EPTC, malathion,

methomyl, naled and its breakdown product DDVP, oxydemeton-methyl, permethrin, and simazine. Results of the monitoring are summarized below.

Benomyl was measured in Kern County in February 1988 using charcoal sorbent and analyzed by high performance liquid chromatography (Baker *et al.*, 1996). Five sites were measured over the course of 13 days and five percent of samples had concentrations that were above the minimum quantitation level of 50 ng/m³. The maximum concentration was 60 ng/m³, and the mean urban background⁵ concentration was 160 ng/m³.

Chlorothalonil was measured in Ventura County in January and February 1990 using charcoal sorbent and analyzed by gas chromatography (Baker *et al.*, 1996). Three sites were measured over the course of 15 days and 7 percent of the sample concentrations were above the minimum quantitation level of 3.9 ng/m³. The maximum concentration was 4.6 ng/m³, the average was 4.4 ng/m³, and the mean urban background concentration was <3.9 ng/m³.

Chlorpyrifos and its oxygen analog were measured in Tulare County during May and June 1996 using XAD-4 resin and gas chromatography (California Air Resources Board, 1998b). Four sites were measured over the course of 22 days and 74 percent of the sample concentrations were above the minimum quantitation level of 9.4 ng/m³. The maximum concentration was 815 ng/m³, and the mean urban background concentration was 27 ng/m³. For chlorpyrifos oxon, 70 percent of the sample concentrations were above the minimum quantitation level of 9.4 ng/m³. The maximum concentration was 230 ng/m³, and the mean urban background concentration was 20 ng/m³.

Diazinon was measured in Fresno County during January and February 1997 using XAD-2 resin and gas chromatography (California Air Resources Board, 1998a). Four sites were measured over a six-week period and 22 percent of the sample concentrations were above the estimated quantitation limit of 215 ng/sample. The estimated quantitation limit, expressed in units of ng/m³, is dependent on the volume of air sampled, which varies from sample to sample. For a 24-hour sampling period at 2 L/min the estimated limit of quantitation would be 75 ng/m³. The maximum concentration was 290 ng/m³, and all urban background sample concentrations were below the level of quantitation.

EPTC was measured in Imperial County during October and November 1996 using XAD-2 resin and gas chromatography (California Air Resources Board, 1998c). Four sites were measured over the course of 24 days and 23 percent of the sample concentrations were above the limit of quantitation of 197 ng/sample. The method limit of quantitation, expressed in units of ng/m³, is dependent on the volume of air sampled, which varies from sample to sample. The method limit of quantitation for a 24-hour sampling period at 1.9 L/min would be 72 ng/m³. The maximum EPTC concentration was 240 ng/m³, and all of the urban background samples had concentrations below the

⁵ The urban background sites used for TAC program monitoring studies are always the largest urban area in the county of monitoring (e.g., Bakersfield when in Kern County, Fresno when in Fresno County, and El Centro when in Imperial County).

limit of quantitation.

Malathion and its breakdown product malaoxon were measured in Imperial County during February and March 1998 using XAD-2 resin and gas chromatography (California Air Resources Board, 1999a). Four sites were measured over the course of 12 days and 78 percent of the sample malathion concentrations were above the estimated quantitation limit of 17.3 ng/sample. The estimated quantitation limit, expressed in units of ng/m^3 , is dependent on the volume of air sampled, which varies from sample to sample. For a 24-hour sampling period at 3 L/min the air concentration would be 4 ng/m^3 for malathion and 7.9 ng/m^3 for malaoxon. The maximum malathion concentration was 90 ng/m^3 , and the mean urban background concentration was 5.7 ng/m^3 . For malaoxon, 37 percent of the sample concentrations were above the estimated quantitation limit. The maximum malaoxon concentration was 28 ng/m^3 , and the mean urban background concentration was 4.8 ng/m^3 .

Methomyl was measured in Fresno County in August 1987 using XAD-2 and high performance liquid chromatography (Baker *et al.*, 1996). Five sites were measured over the course of 14 days and all the concentrations were less than the minimum quantitation level of 20 ng/m^3 .

Naled/dichlorvos (DDVP) were measured in Tulare County during May and June 1991 using XAD-2, and analyzed by gas chromatography (Baker *et al.*, 1996). Four sites were measured over the course of 16 days and 14 percent of the sample concentrations were above the minimum quantitation level of 40 ng/m^3 . The maximum concentration was 65 ng/m^3 , and the mean urban background concentration was 68 ng/m^3 .

Oxydemeton-methyl was measured in Monterey County during August and September 1995 using XAD-4 resin, and analyzed by gas chromatography (California Air Resources Board, 1996). Five sites were measured over the course of 15 days and none of the sample concentrations were above the limit of quantitation. The limit of quantitation for oxydemeton-methyl and its breakdown product was 250 ng/samples (12 ng/m^3 for a 24-hour sample collected at 14.6 L/min).

Permethrin was measured in Monterey County during August and September 1997 using XAD-4 resin and gas chromatography (California Air Resources Board, 1998d). Four sites were measured over the course of 24 days and 5 percent of the sample concentrations were above the limit of detection, but were below the limit of quantitation; the remaining sample concentrations were below the limit of detection. All urban background samples had concentrations below the limit of detection. The limit of quantitation for permethrin was 330 ng/sample. The air concentration, expressed in units of $\mu\text{g}/\text{m}^3$, associated with the limit of quantitation is dependent on the volume of air samples, which varies from sample to sample. For a 24-hour sampling period at 15 L/min the air concentration would be 15 ng/m^3 as associated with the limit of quantitation.

Simazine was measured in Fresno County during February through April 1998 using

XAD-2 resin and gas chromatography (California Air Resources Board, 1999b). Four sites were measured over the course of 24 days and 18 percent of the sample concentrations were above the estimated quantitation limit. The analytical estimated quantitation limit for simazine was 18.2 ng/sample. The air concentration, expressed in units of ng/m^3 , with the associated estimated quantitation limit is dependent on the volume of air sampled, which varies from sample to sample. For a 24-hour sampling period at 3 L/min the air concentration would be $4.2 \text{ ng}/\text{m}^3$ for simazine as associated with the estimated quantitation limit. The maximum concentration was $18 \text{ ng}/\text{m}^3$; all background sample concentrations were below the estimated quantitation limit.

5. SAMPLE COLLECTION DESIGN

The design for sample collection is a product of the DQO process as well as a result of community and technical input from the TAG and LIWG. This section describes the types of samples to be collected, sample measurement details, numbers of sampling sites and their general location, and other information pertinent to field collection and shipment of samples.

5.1 Safety

Sampling of air in the city of Lompoc does not pose an occupational hazard for the sampling crew. However, a concern exists for sampling crew safety. Air samplers are located on rooftops for sample security purposes and access to the roofs is by ladder. Due to the lack of safety guardrails on the rooftops, air sample changes will be restricted to daylight hours. It takes approximately two hours to change the tubes at four sites. For that reason, air sample changes during this study will be conducted during daylight hours at the same time each sample change.

An additional safety consideration is sampling during rainfall events. Due to slick surface conditions on rooftops and the lack of guardrails, sampling will not be conducted when it rains. In the event of a light rain or drizzle, field-sampling staff will proceed with sampling if they are confident it is safe to do so.

5.2 Sampling Theory

In Phase One sampling, five sites were used to monitor air concentrations in Lompoc. In discussion with the TAG on October 26, 1999, the fumigant sampling plan was formulated based on study objectives and monetary constraints. The TAG decided to monitor the original five sites. However, due to monetary constraints of this study, the TAG modified the number of sites to include four of the original five sites. The sites of primary concern were those along the western edge of the city due to proximity to the majority of the agriculture in the valley and the predominance of wind directions from the west and northwest. Therefore, the TAG recommended 10 consecutive weeks of monitoring the first group of chemicals during their highest expected use period, four days per week, in an attempt to capture peak air concentrations to which residents in Lompoc might be exposed. The second group of chemicals will be monitored at a later

time, during their expected high use period.

DPR asked the TAG to prioritize a variety of options for this multiple-pesticide sampling and analysis plan. On January 20, 2000, the LIWG agreed to pursue monitoring 23 pesticides and 5 breakdown products that can be analyzed by gas chromatography in a single analysis at the University of California, Davis (UCD) (Group 1). For this component, DPR would monitor for 10 consecutive weeks at 4 sites, collecting samples 24-hour in duration 4 days/week (total of 160 samples) for the chemicals shown in Table 4. This list does not include one chemical included in Phase One: disulfoton. The approximate cost for this component follows.

Field Sampling	\$1500 X 10 wks	\$15,000
Method Development	\$25,000	\$25,000
Sample Analysis	160 samples X \$730/sample	\$116,800
Quality Control	8 samples/wk X 10 wks X \$730/sample	\$58,400
TOTAL		\$215,200

CDFA component: CDFA will serve as the confirmation laboratory for the UCD primary lab. CDFA will analyze collocated samples for 4 chemicals, including chlorpyrifos, diazinon, dimethoate, and malathion as part of the quality control program. DPR will absorb these costs.

Meteorology component: DPR has allocated \$20,000 toward the LIWG's Other Environmental Issues Subgroup meteorology study, which supplements other funds from U.S. EPA, the City of Lompoc, and Santa Barbara County.

DPR suggested several options for the remaining funds (\$100,000) and asked for the TAG's review. The TAG has chosen the following option: Liquid chromatography/mass spectroscopy (LC/MS) method development by Battelle. This option will develop a method to analyze up to 9 pesticides and 2 breakdown products (Group 2 chemicals, Table 5), mostly carbamates. Other options that were considered, but rejected, are included in Appendix G.

5.3 Sampling Method

This section will describe a field-sampling method that will be used to measure air concentrations of the pesticides. The method uses sorbent cartridges to trap the pesticides and sampling and chemical analytical methods that have been established for all pesticides.

5.3.1 Sorbent Cartridges

The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute through a solid sorbent material onto which the pesticide is adsorbed (Keith, 1988). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel, 1995; Keith, 1988;

Baker *et al.*, 1996). Each sampling cartridge will contain 30 mL of XAD-4 for the field samples. The expected flow rate will be 15 L/min.

5.4 Sample Type

Air samples will be run for a consecutive 24-hour period. For safety reasons, the change of air sampling cartridges will occur in daylight hours. The daytime sample will commence at the same time each day at the first site. This sequence of air sampling tube changes will continue until four days have been completed (96 hours of sampling).

5.5 Media

In addition to air samples, meteorological measurements of wind speed, wind direction, temperature, and relative humidity will be made. See Section 5.14 for meteorological sampling details.

5.6 Collection Schedule

As many of the candidate compounds in Group 1 as possible will be monitored during late May, June, July, and early August (Group 1; Table 4), depending on when sample collection begins. Up to 11 compounds will be monitored during September (Group 2; Table 5). For the first group of pesticides monitored (Table 4), four sequential samples, 24-hour in duration, will be collected each week for 10 consecutive weeks at each site, as described in 5.3 above. However, since oxydemeton-methyl cannot be analyzed as part of this multiple-pesticide analysis, UCD has developed a single pesticide analysis for it. This single pesticide analysis adds additional cost to the project; therefore, separate samples of oxydemeton-methyl, 24 hours in durations, will be collected for four days per week for the last two weeks of this sampling period at two sites. For the second group of pesticides monitored (Table 5), four sequential samples, 24-hour in duration, will be collected each week for at least 3 consecutive weeks at each site, as described in 5.3 above.

5.6.1 *Schedule for Quality Control Field Sampling*

In addition to field samples collected during monitoring, two fortified field spikes, one trip spike, one trip blank, one (co-located) duplicate, and two (co-located) confirmation samples will be collected each 4-day sampling event.

A fortified spike is a laboratory spike, which is sent to the field and placed on an air sampler with air flowing through the sorbent cartridge. Shipped overnight on dry ice to the field, it is treated just like a field sample, including storage and shipping conditions. The fortified spike, in comparison with trip spikes and the respective field sample, gives us some information about any change in our ability to recover the analyte during air sampling.

The trip spikes will be generated in the primary laboratory, at a concentration within the

range of concentrations anticipated. The trip spike shipped overnight to the field technician will be stored on dry ice until all samples for the 4-day sampling event are collected. The trip spike will be sent back to the primary laboratory with the field samples for analysis.

The cartridges used for trip blanks will be sent with the spikes from the laboratory. These cartridges will be taken from the same storage shed where all other sampling cartridges are kept prior to use. The trip blank will be stored on ice until all samples are collected. The trip blank will be shipped overnight with the field samples to the primary laboratory for analysis.

A duplicate sample is a sample that is co-located with a field sample. The primary laboratory will analyze the duplicate samples. These samples serve to evaluate overall precision in sample measurement and analysis.

A confirmation sample is a sample that is co-located with a field sample, yet analyzed by the confirmation laboratory. Two confirmation samples will be shipped to the confirmation laboratory for analysis.

The site and time of duplicate sampling, fortified sampling, and confirmation sampling was randomly assigned.

5.7 Sampling Site Locations

Monitoring will occur at four sites within the city of Lompoc, one each in the northwest, central-west, southwest, and near the center of Lompoc (Figure 3). These sites were also used for Phase One, and for the Phase Two/Fumigant Sampling and Analysis. All locations meet the U.S. EPA siting criteria for ambient air monitoring sites (Appendix F). Samplers at all locations are on rooftops to ensure the security of the samples. As an extra measure of security, members of the TAG requested that the exact street address of these sites not be included in sampling-plan documents.

5.8 Preparation for Sampling

Sample labels with the study number and sample identification number will be attached to all sampling cartridges. Chain of custody forms and log book entry forms will be supplied to field sampling staff. Samplers will be pre-calibrated in the laboratory for the flow rates required for air sampling. Permission for access to sampling sites will be confirmed at all four locations. A storage unit will be rented to house equipment and samples temporarily stored on dry ice. All equipment necessary for monitoring will be delivered to Lompoc and set up prior to pesticide air monitoring.

A MetOne® meteorological station will be placed approximately one mile west of Lompoc (Figure 1). The station will be operational prior to the start of monitoring. Meteorological data will be collected during the course of the entire monitoring period (late May through early August, and September).

5.9 Equipment

Equipment to be delivered to field sampling staff

Log Book Entry Forms
Andersen air pumps
Tubing
Sampler support system
Rotameters
Flow Calibrators
Sample XAD-4 cartridges
Sample labels
Ziplock bags (for storing individual samples and labels in the ice chest following sampling)
Chain of custody forms
MetOne® meteorological station
Campbell Scientific micrologger and storage modules
Compass
Allen wrenches
Spanner wrench
Anemometer
Sling psychrometer
Hand-held Thermometer
Hobo Temp Temperature Data loggers
Ice chests or freeze-safes
Duct tape
Dry ice (to be purchased as needed)

5.10 Field Tests

Prior to field sampling, DPR personnel will meet with the technician collecting the samples in Lompoc to discuss the sampling procedure. An on-site demonstration of the sampling procedure will be conducted. Sample storage, shipping and paperwork will be addressed before actual sampling begins.

The MetOne® meteorological station will be checked once a month against hand-held sensors (Appendix H). Storage modules will be exchanged and downloaded approximately once a month.

Air sampling pumps will be calibrated in the laboratory prior to monitoring. In addition, flow rates will be checked in the field before and after each sampling interval with a rotameter (Appendix H). Rotameters are checked against a flow calibrator in the laboratory.

5.11 Field Testing Procedure References

The use, operation, calibration and maintenance of Andersen air sampling pumps are described in DPR's SOP EQAI001.00 (Appendix H). Preparation and usage of temperature data loggers that are placed in ice chests to record temporary storage and transport temperatures are described in DPR's SOP EQOT001.01 (Appendix H). The meteorological station will be set up according to DPR's SOP EQWE001.00 (Appendix H).

5.12 Sample Collection References

Sorbent cartridge samples will be collected according to procedures listed in DPR SOP EQAI001.00 (Appendix H). Instructions for field sampling personnel are detailed in DPR's protocol for air monitoring in Lompoc (Appendix I). Chain of custody forms and log book entry forms are appendices in DPR's air monitoring protocol (Appendix I).

5.13 Shipment of Samples

FedEx will ship samples overnight. The samples will be packaged and shipped according to procedures in DPR's SOP QAQC004.1 (Appendix H). UCD and CDFA samples will be sent in separate ice chests, directly to the lab. Battelle samples will be sent in an ice chest directly to the lab. Each lab will have chain of custody forms. Each shipment of samples will be accompanied by a temperature data-logger to record sample temperatures from collection to delivery to the lab. Shipment of samples will be scheduled weekly. DPR will arrange sample shipment such that samples will arrive in the laboratory on a weekday when possible, not on a weekend or holiday. Based on UCD's and CDFA's preference, samples will be delivered directly to the lab or will be picked up from FedEx at the Sacramento Airport. Samples will be delivered directly to Battelle.

The Lompoc technician will ship samples in individual sealed plastic bags each containing a label for the individual samples.

Upon shipping samples from Lompoc to the primary laboratory, DPR has asked the Lompoc technician to fax a sample list to alert the primary lab of the number of samples being shipped: UCD's fax number is (530) 754-8556, and Battelle's fax number is (614) 424-3557. Neither DPR nor CDFA desire such notification.

Oxydemeton-methyl samples will be collected during the last two weeks of monitoring for Group 1 pesticides. Samples that require analysis of oxydemeton-methyl will be in separate plastic bags, labeled oxydemeton-methyl.

5.13.1 DPR Sampling Contacts

DPR's primary and back-up contacts for sampling are listed below:

Primary Contact: Pam Wofford, Field Coordinator
Associate Environmental Research Scientist

Department of Pesticide Regulation
Environmental Monitoring & Pest Management Branch
830 K Street
Sacramento, CA 95814
Telephone: (916) 324-4297
Facsimile: (916) 324-4088
E-mail: pwofford@cdpr.ca.gov

Back-up Contact: Randy Segawa, Project Leader
Senior Environmental Research Scientist
Department of Pesticide Regulation
See above for mailing address
Telephone: (916) 324-4137
Facsimile: (916) 324-4088
E-mail: rsegawa@cdpr.ca.gov

5.14 Meteorological Sampling

A MetOne® meteorological station will be set up at a site near the agricultural areas on the west side of the city of Lompoc. The station will be set up according to DPR's SOP EQWE001.00 (Appendix H). The MetOne® meteorological sensors will be placed on a trailer mast at a height of 10 meters. The sensors will record wind direction, horizontal wind speed, temperature, and relative humidity. The manufacturer calibrated the MetOne® sensors on October 5, 1999 to fit within the specifications of the manufacturer. The meteorological data will be recorded on a Campbell Scientific CR 21X Datalogger every 15 minutes as per U.S. EPA Guidelines on air quality models (revised), (see Appendix W of 40 CFR part 51 EPA-450/2-78-027R).

5.15 Pesticide Use Data

Pesticide use data will be collected from pesticide use reports submitted by growers to the County Agriculture Commissioner's Office. Universal use reporting, required by the state of California, directs all growers to submit details of pesticide usage on a monthly basis.

As part of general enforcement procedures, staff from the Agriculture Commissioner's Office are required by law to perform inspections of 5% of all sites identified in permits or notices of intent to apply a pesticide for an agricultural purpose (3 CCR 6436). These inspections are performed on a non-appointment basis and cover various aspects of pesticide use such as compliance with permit and label requirements, application equipment inspections, mix/load inspections, and field-worker safety inspections. Department of Pesticide Regulation manual (DPR 1997b) details procedures that enforcement staff use to assure grower compliance with pesticide labels and state and federal laws regarding pesticide use.

6. SAMPLE ANALYSIS DESIGN

6.1 Constituents of Interest

So far, the LIWG has identified the pesticides shown in Tables 4 and 5 as the constituents of interest. These lists include breakdown products of the pesticides acephate, chlorpyrifos, diazinon, dimethoate, fonofos, malathion, and naled. These degradation products have been theorized or actually measured in air (Wales, 1999; Moilanen *et al.*, 1978; Woodrow *et al.*, 1983; Carter *et al.*, 1997). However, due to budgetary constraints, air measurement of additional atmospheric constituents (i.e., other breakdown products) cannot be addressed in this study.

6.2 Sample Preparation References

Chemical extraction methods for these gas chromatography and liquid chromatography/mass spectroscopy pesticides from sorbent cartridges are referenced below for the primary and confirmation laboratories.

6.2.1 Chemical extraction methods for pesticides from sorbent cartridges analyzed by GC

The primary laboratory – Appendix J describes the chemical extraction method for pesticides from sorbent cartridges.

The confirmation laboratory – Appendix K describes the chemical extraction method for pesticides from sorbent cartridges. [Note: This information will be included when it is available.]

6.2.2 Chemical extraction methods for pesticides from sorbent cartridges analyzed by LC/MS

The primary laboratory – Appendix L describes the chemical extraction method for pesticides from sorbent cartridges. [Note: Since Battelle is currently developing methods, this information is not available. Prior to sample analysis, they will supply this information and it will be included.]

6.3 Analysis Procedure References

Chemical analytical methods for these pesticides from sorbent cartridges are referenced below for the primary and confirmation laboratories.

6.3.1 Chemical analytical methods for pesticides extracted from cartridges analyzed by GC

The primary laboratory – Appendix J describes the analytical methods for pesticides extracted from sorbent cartridges.

The confirmation laboratory – Appendix K describes the analytical methods for

pesticides extracted from sorbent cartridges.

6.3.2 Chemical analytical methods for pesticides extracted from sorbent cartridges analyzed by LC/MS

The primary laboratory – Appendix L describes the analytical methods for pesticides extracted from sorbent cartridges.

6.4 Initial Quality Control Requirements

Initial quality control consists of a standards check, verification of calibration, the method detection limit determination, and analysis of matrix spikes.

6.4.1 Standards Check

Each laboratory uses certified standards. The primary (UCD) and quality control (CDFA) laboratories will exchange standards for chlorpyrifos, diazinon, diazinon oxon, dimethoate, malathion, and malathion oxon for verification. New standards are prepared at least every six months. New standards are compared with old standards for verification. Standards for pesticides have shown no degradation over a six-month period in prior studies.

DPR, UCD and CDFA labs have agreed that all three parties should know the date of the exchange of standards and a date by which the laboratories are to report results to DPR. DPR has scheduled the date of the exchange of standards, and the date by which laboratories are to report results to DPR. The laboratories have conducted the exchange of standards and completed the standards check. DPR has both laboratories' results of the analysis of the other laboratory's standards. DPR has provided these results to both laboratories and to the Quality Assurance team (see Appendix M).

6.4.2 Verification of Calibration

Both the primary and quality control laboratories verify calibration by analyzing a series of standards (samples containing known amounts of analyte dissolved in a solvent for the sorbent samples). The linear range of calibration is determined by analyzing standards of increasing concentration. Within the linear range, the calibration is determined by regressing the standard concentration on the response of the instrument (peak height or peak area of the chromatogram) using at least five concentrations. The minimum acceptable correlation coefficient of the calibration is given in the SOP for each method, but in general is at least 0.95. The calibration is verified with each set of samples analyzed as described in section 6.4 for continuing quality control.

6.4.3 Method Detection Limit and Limit of Quantitation

Each laboratory determined the method detection limit for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. The spiked matrix is

analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990). The method detection for each analyte and method is given in the SOP.

The limit of quantitation is set a certain factor above the method detection limit. The level of interference found in the samples determines this factor: the more interference, the higher the factor. The limit of quantitation for each analyte, along with a summary of chemical analytical and air sampling methods, can be found in Table 16.

6.5 Laboratories

The primary laboratory for all Group 1 analytes (Table 4) is the Trace Analytical Laboratory, Department of Environmental Toxicology, University of California, Davis, California 95616. Its confirmation laboratory is the California Department of Food and Agriculture, Center for Analytical Chemistry located at 3292 Meadowview Road, Sacramento, California 95832.

The primary laboratory for all Group 2 analytes (Table 5) is Battelle Atmospheric Science and Applied Technology Department, 505 King Avenue, Columbus, Ohio 43201-6424. A confirmation laboratory will not be used.

6.6 Sample Transit Conditions

Immediately following sample collection, all air samples collected using sorbent cartridges will be placed in a cooler or freeze safe containing ample quantities of dry ice (see Section 5.12 for details of sample shipment conditions). Upon arrival in the analytical laboratories and after sample check-in procedures, samples will be placed in secure freezers kept at -4°C or below.

6.7 Holding Times

Sample holding will be determined for each analyte using storage stability measurements performed in the laboratory (see Appendices J and L for data on storage stability) (Table 17).

6.8 Trapping Efficiency

When available, each primary laboratory (i.e., UCD and Battelle) will provide the trapping efficiency for each pesticide trapped on sorbent cartridges (see Appendices J and L) (Table 17).

7. DATA VALIDATION/QUALITY ASSURANCE

7.1 Sample Receipt Verification

Sample receipt, log-in, and verification procedures for each laboratory exist.

7.2 Holding Time Verification

Holding times will be verified by date of sample collection and date of extraction listed on the chain of custody records and laboratory reports. Verification will be ensured in the laboratory by the lead chemist assigned to the project and also checked by the project leader at DPR.

7.3 Audit Results

The quality assurance (QA) team for this project, led by staff from the California Air Resources Board, will submit a questionnaire to all three laboratories participating in this study. Subsequent to mailing this questionnaire, the QA team will visit the UCD laboratory for an audit prior to study commencement (Appendix N). To evaluate Battelle in Ohio, the quality assurance questionnaire will be sent to Battelle. The quality assurance team will conduct a phone interview with Battelle to evaluate their responses to the questionnaire. The audit will result in a list of items that will assist the laboratories in their efforts to have quality data. [Note: The QA team has conducted an audit of the CDFA laboratory within the past six months. A pre-study audit is not necessary for this laboratory.]

In addition, the QA team will schedule another audit during sample analysis for each laboratory. A review of raw data and laboratory tracking procedures will be conducted on a minimum of 5% of all samples collected. In addition, an audit of the five highest concentrations will be conducted. Due to its out-of-state location, the QA team will not conduct an on-site audit of Battelle.

In addition, attempts will be made to include a field audit, to verify air sampler flow rates, as part of the quality assurance evaluation.

7.4 Quality Control Results

A five-point calibration curve, minimum, will be run in each laboratory (UCD, CDFA, and Battelle) with each extraction set. The five points shall span the linear range of the method.

Each of the three laboratories will generate new stock solutions and working standards at least every six months.

At UCD, continuing quality control samples will be run each week with each extraction set and will include three matrix spikes at one level, and one laboratory blank. Levels will alternate over the weeks and will include concentrations that are 1, 2, 3, 4, and 5 times the estimated quantitation limit. Matrix spikes will be performed in both the primary (UCD) and confirmation (CDFA) laboratories using the same procedure (i.e., matrix spikes will be made directly into the sorbent cartridges and then extracted). At CDFA, continuing quality control samples will be run each week with each extraction set and will include one matrix spike at one level (about 2-3 times the reporting limit) and

one laboratory blank (Appendix O).

If recovery for continuing quality control spikes is greater than 70 and less than 120 %, then no action is indicated. However, when percent recovery is less than 70 or greater than 120, then UCD will notify DPR's Project Leader.

For Group 1 compounds (Table 4): Mass spectroscopy is the preferred method for confirmation of such compounds. Positive samples will be confirmed using mass spectroscopy. However, the mass spectroscopy detection limit is higher than the limit of quantitation for the primary method (gas chromatography), so only samples with a concentration higher than the gas chromatography limit of quantitation can be confirmed with mass spectroscopy. Therefore, the primary laboratory (UCD) will confirm positive organophosphate samples when the concentration is more than five times the estimated limit of quantitation of the gas chromatography method. In addition, the confirmation laboratory (CDFA) was established to confirm 10% of all samples collected. Where mass spectroscopy is used, intra-laboratory confirmation will not be required since this is a definitive method.

Spikes and blanks returned to the laboratory from the field will be blind, i.e., analyte content will be unknown. Spikes and blanks will arrive with field samples, look like field samples, and their content will be unknown to the chemist.

The following describes trip spikes and fortified spikes to be generated for each 4-day sampling event by the primary laboratory for sorbent cartridges. One trip spike will be prepared for each 4-day sampling event. Trip spikes shall be sent overnight mail, on dry ice, to the field sampling staff address provided. Once received by field staff, all appropriate paper work and sample storage conditions will be met as described above in Section 5. Trip spikes must be kept on dry ice as field staff continues with sample collection.

Trip spikes should have recoveries equivalent to the recoveries found during method validation. This information will be available later in the project.

In addition to trip spikes, two fortified (sample) spikes will be generated by the primary laboratory and mailed with the trip spikes. A fortified spike is a spike that is mounted on an air sampler and run on an air sampler just like a field sample. The fortified spikes will be spiked at two to five times the estimated quantitation limit.

In addition to spikes, one trip blank will be prepared per 4-day sampling event by the field technician. The trip blanks will be returned to the primary laboratory.

Trip blanks and laboratory blanks should not contain the analytes measured (i.e., all below the method detection limit). Any deviation from this will first be investigated in the laboratory to determine if a contamination problem exists. If a contamination problem is identified, UCD will notify DPR's Project Leader. Any adjustments to the data, if made at all, will be fully disclosed in the final report. Other sources of

contamination will be investigated if laboratory contamination is ruled out, e.g., contamination during shipping.

All data reported shall go through review in the laboratory, in accordance with each laboratory's quality assurance plan or SOP, prior to submission to DPR. Signatures of the supervising chemist and/or analytical chemist(s) will verify that this review has occurred.

7.5 Laboratory Reporting

The laboratory reports shall include at a minimum, the following information:

- Analytical results for all samples, trip spikes, fortified spikes, field blanks in $\mu\text{g}/\text{sample}$. Dates of extraction and analysis will be recorded for each sample.
- Mass spectroscopy confirmation will be reported, if performed.
- Case narrative (UCD will notify DPR by telephone of any problems encountered).
- Chain of custody
- Sample receipt (Log-in) forms
- Blank sample results
- Matrix spike results and identification of corresponding samples in the same extraction set
- Condition of samples upon receipt by laboratory
- Date of sample receipt
- Date of sample extraction
- Date of sample analysis

8. DATA ANALYSIS

8.1 Calculation of Air Concentrations

Twenty-four-hour air concentrations will be calculated from the weight of analyte per sample (determined in the chemical analysis) divided by the volume of air drawn through an air sampler during the corresponding sampling period. Concentrations will be reported in $\mu\text{g m}^{-3}$ and also converted to parts per billion, volume per volume. Samples below the limit of detection will be treated as having one-half the detection limit.

Subchronic exposures will be calculated by averaging the eight highest 24-hour concentrations measured at each site.

Annual average air concentrations will be approximated using the Pesticide Use Report data as follows. Monthly average concentrations for each pesticide will be calculated by averaging all monitoring samples taken within two calendar months. Total pounds of the pesticide applied will be determined for that period and for each two-calendar-month period of the preceding 10 months. Total pounds applied in each two-month period will be expressed as a fraction of the total pounds applied during the monitoring period. Average air concentration in each nonmonitored period will be assumed to equal the corresponding fraction of the air concentration in the monitored period. The six two-

month concentrations will be averaged to yield an average annual concentration.

Thus, the annual average will be calculated as

$$(1/6)A^3 [(LBS_i/LBS_m)A C_m] = C_m A (3 LBS_i)/(6 A LBS_m),$$

where LBS_i and LBS_m are the total pounds applied during calendar period i and the monitoring period, respectively, and C_m is the average of all air samples taken during the monitoring period.

Use and air concentrations will also be examined for shorter intervals to determine whether a correlation (possibly lagged) exists. If it does, the approximation just described will be done for the shorter interval. In the event that no correlation can be found between use and concentration, the approach used in the Toxic Air Contaminant program will be used: the annual concentration will be calculated as the overall mean concentration during monitoring times the fraction of the year in which the pesticide is used (i.e., if there is use in 7 months of the year, concentration is multiplied by 7/12).

8.2 Estimate Total Error

Sampling design error – The sampling variances of the sample maximum and the maximum 8-day average will be estimated by computer simulation, using the parameter values estimated from the data and assuming lognormality of the underlying distribution.

Measurement error – Total measurement error is captured in the variability within pairs of colocated duplicate samples. After data collection is complete, this variance will be estimated as the within-pairs mean-squared-error in a between-pairs analysis of variance.

Total error – Total error variance will be estimated as the sum of the variances estimated for sampling and measurement error. A total error coefficient of variation will be calculated for each pesticide as the square root of total error variance divided by the overall mean pesticide concentration. In Phase One, the total error CV for chlorpyrifos was 840 % (Phase One overall mean = 5.9 ng/m^3 ; within-pairs MSE based on 20 colocated pairs = 2.11×10^{-6} ; the variance of the maximum of 120 samples simulated from a lognormal distribution with mean and standard deviation of 6 and 10.5 ng/m^3 , respectively, was 2.45×10^{-3}).

For annual average concentration, the total error of the function in 8.1 will be approximated from the variances of its components using computer simulation. Total error of C_m will be estimated as the sum of the observed variance of all samples plus measurement error (as estimated in the paragraph above), divided by the total number of samples. Total error in the ratio of pounds applied per year to pounds applied during the monitoring period will be the observed variability of that ratio over the past five years. In addition, there is a prediction error in assuming air concentration is proportional to use; without data to estimate this error, we will have to assume a value (e.g., plus or minus 100%).

8.3 Statistical Evaluation

The null hypothesis for acute exposure is that the maximum 24-hour air concentration is greater than or equal to the acute screening level. The null hypothesis will be rejected if the maximum 24-hour air concentration observed for the pesticide is less than the $\nabla = 0.10$ critical value. The critical value for testing the null hypothesis for each pesticide will be determined after the final screening levels are established.

The null hypothesis for subchronic exposure is that the maximum 8-day average concentration is greater than or equal to the subchronic screening level. The null hypothesis will be rejected if the maximum 8-day average concentration of the pesticide observed at any site is less than the $\nabla = 0.10$ critical value. The critical value for testing the null hypothesis for each pesticide will be determined after the final screening levels are established.

No statistical test will be done for the annual average concentration. The value will simply be compared to the final screening level.

8.4 Weather and Pesticide Use

The date, location, number of acres treated and pounds of ai applied will be tabulated for every pesticide application from May 2000 through the end of the monitoring. Average daily weather conditions during the applications will also be tabulated, including temperature, precipitation, humidity, wind speed and wind direction (hours per day from each direction). Application and weather characteristics during the monitored applications will be compared qualitatively to those of nonmonitored applications. The objective of this comparison is to determine whether the monitored applications were typical of all applications in the season, and whether the maximum concentration was likely to have been captured. In addition, the application and weather characteristics of applications during the monitoring period will be compared to those of previous years, to assess whether the 2000 application season was similar to previous application seasons and years. Overlay maps of pesticide use and weather conditions may be prepared to assist in this comparison.

9. PROJECT ORGANIZATION

DPR's standard project organization and responsibilities are described in SOP ADMN002.00 (Appendix P). This project is under the overall management of John Sanders. Other key personnel assigned to this project include:

Project Leader:	Randy Segawa, DPR
Assistant Project Leader:	Madeline Brattesani, DPR
Senior Scientist:	Jim Sanborn, DPR
Field Sampling Coordinator:	Pam Wofford, DPR
Statistician:	Sally Powell, DPR

Chemical Analysis:	<p>Chuck Mourer⁶, Trace Analytical Lab, Dept. of Environmental Toxicology, University of California, Davis</p> <p>Donald Kenny, Battelle Atmospheric Science and Applied Technology Department</p> <p>Cathy Cooper, CA Dept. Food and Agriculture</p>
Quality Assurance:	<p>Don Fitzell, Air Resources Board</p> <p>Carissa Ganapathy, DPR</p>

In addition, to the personnel described above and in SOP ADMN002.00, other people have key roles for this specific project. DPR formed the LIWG to assist with the project. The LIWG consists of staff from federal, state, county and city agencies, as well as community representatives. The LIWG advises DPR on overall project goals, priorities, and funding. The LIWG includes several subgroups. One of those subgroups, the TAG, assists DPR in the planning of pesticide air monitoring and evaluation of results.

DPR is normally responsible for all quality assurance functions for its projects. For this project, DPR formed a multi-agency quality assurance team to assist with these functions. Don Fitzell, Air Resources Board, leads the multi-agency quality assurance team. This team is responsible for auditing field and laboratory procedures (as specified in the above plan), and providing a report of their audit findings to DPR management. DPR is responsible for all other quality assurance functions described in SOP ADMN002.00 (Appendix P).

A flow diagram shows the project organization (Figure 5).

ACKNOWLEDGEMENTS

Thank you to all members of the TAG for comments on the draft sampling and analysis plan dated May 22, 2000. The above text reflects those helpful comments and suggestions. Comments, and DPR's response to those comments, can be found in Appendix Q.

We also would like to acknowledge the assistance of the following individuals from DPR: Randy Segawa for his overall direction on this project, Lisa Ross for providing the framework for this plan, Donna Bartkowiak for pesticide use reporting data, Wynetta Kollman for physical and chemical data about candidate pesticides, Jim Sanborn and Carissa Ganapathy for their technical reviews and Lynn Baker, of the Air Resources Board, for providing information on particulate sampling.

⁶ If unavailable, please contact Matt Hengel.

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Table 1. Pesticides with the largest increase in use in the Lompoc area between 1995 and 1998

CHEMICAL	1995 (lbs)	1998 (lbs)
NAPROPAMIDE	0	1,243
CRYOLITE	0	554
SPINOSAD	0	411
MEFENOXAM	0	359
CYCLOATE	0	288
ANILAZINE	0	131
PROPICONAZOLE	0	125
PCNB	9	2,834
NALED	73	515
DIAZINON	125	700
METOLACHLOR	139	698
IMIDACLOPRID	49	212
BENSULIDE	314	1,039
THIOPHANATE-METHYL	263	834
GLYPHOSATE, ISOPROPYLAMINE SALT	814	2,097
ESFENVALERATE	49	114
ALACHLOR	421	947
TRIFLURALIN	78	174

Table 2. Pounds of pesticides used in agricultural production in the Lompoc area, 1996-1998.

Pesticide	1996	1997	1998	Total
METAM-SODIUM	11251.48	34972.47	51831.75	98,056
FOSETYL-AL	15840.7	14664.4	15818.92	46,324
SULFUR	7137.896	10193.79	8203.22	25,535
MANEB	7368.164	8784.945	9130.043	25,283
CHLORTHAL-DIMETHYL	6804.356	6601.215	3526.785	16,932
IPRODIONE	4964.377	4682.179	4534.918	14,181
METHYL BROMIDE	680.7	970.94	12150	13,802
CHLORPYRIFOS	4552.84	4669.814	2916.618	12,139
GLYPHOSATE, ISOPROPYLAMINE SALT	1543.56	6766.711	2097.233	10,408
ACEPHATE	2921.129	2675.693	2381.912	7,979
PROPYZAMIDE	2123.604	2586.852	2294.49	7,005
CHLOROTHALONIL	3593.292	1242.528	1843.433	6,679
DICLORAN	2291.745	2062.995	1896.233	6,251
PERMETHRIN	2150.77	2127.659	1723.291	6,002
METHOMYL	1932.318	3022.38	973.917	5,929
1,3-DICHLOROPROPENE		5849.675		5,850
CHLOROPICRIN	1.5	91.06	4050	4,143
PCNB	54.8925	550.125	2833.883	3,439
THIODICARB	1395.478	1760.928	74.81656	3,231
MANCOZEB	1230.71	996.9681	1001.203	3,229
CRYOLITE	1511.76	820.8	553.68	2,886
VINCLOZOLIN	904.6569	869.5609	900.1268	2,674
OXYDEMETON-METHYL	729.0134	989.0645	882.8147	2,601
BENSULIDE	62.11403	1425.133	1038.524	2,526
OXAMYL	1188.022	749.433	460.997	2,398
ALACHLOR	951.1082	482.0543	946.6817	2,380
NAPROPAMIDE	812	207.75	1243	2,263
MALATHION	1273.755	509.0011	357.5424	2,140
DIAZINON	524.6667	903.221	700.0227	2,128
PROMETRYN	642.1781	592.7105	725.3067	1,960
METALAXYL	1325.726	316.0291	253.2327	1,895
LINURON	446.5	854.45	516.35	1,817
THIOPHANATE-METHYL	335.6063	490.7578	833.91	1,660
METOLACHLOR	407.0736	484.139	697.6708	1,589
2,4-D, DIMETHYLAMINE SALT	413.3978	487.2084	560.9866	1,462
ETHALFLURALIN	637.5556	381.342	385.4798	1,404
DIMETHOATE	199.8054	535.8102	601.0336	1,337
BACILLUS THURINGIENSIS (BERLINER), SUBSP. AIZAWAI, SEROTYPE H-7	603.0032	430.625	183.2638	1,217
FONOFOS	570.1655	282.0818	220.0639	1,072
PIPERONYL BUTOXIDE	433.3684	584.9594	30.05129	1,048
OXYFLUORFEN	230.4558	330.23	393.4902	954
XYLENE RANGE AROMATIC SOLVENT		490.1715	439.5842	930
SIMAZINE	858.88		41.4	900

PETROLEUM OIL, UNCLASSIFIED	797.9724			798
CYCLOATE	215.0958	294.1459	288.4965	798
BENOMYL	364.9657	172.0494	254.736	792
NALED	28.35967	230.5659	514.5604	773
MEFENOXAM		399.6432	358.5404	758
COPPER HYDROXIDE	493.6667	135.7355	118.8798	748
PARAQUAT DICHLORIDE	225.5865	401.4455	101.0509	728
ANILAZINE	388.5	177.5	131.375	697
CYPERMETHRIN	289.5614	288.8128	112.6762	691
IMIDACLOPRID	190.2529	182.1634	211.7425	584
TRIFLURALIN	183.4967	199.4558	174.4786	557
SPINOSAD		138.7733	410.6398	549
BACILLUS THURINGIENSIS (BERLINER), SUBSP. KURSTAKI, STRAIN SA-11	106.4758	266.5539	70.48983	444
BACILLUS THURINGIENSIS SUBSPECIES KURSTAKI, GENETICALLY ENGINEERED STRAIN EG7841	2.025	387.7616	46.5165	436
LEPIDOPTERAN ACTIVE TOXIN				
MYCLOBUTANIL	164.934	155.736	82.0068	403
DICOFOL	287.9147	20.54816	20.04698	329
CARBARYL	209.8	65.58837	37.504	313
ESFENVALERATE	74.45733	117.5329	113.9877	306
NORFLURAZON	292.392	4.716	7.86	305
PIPERONYL BUTOXIDE, TECHNICAL, OTHER RELATED	108.3421	146.2398	7.512821	262
CORN PRODUCT, HYDROLYZED		132.7719	76.92344	210
DISULFOTON	204.5273			205
EPTC	81.06864	39.22676	65.37799	186
PROPICONAZOLE		57.06574	125.3003	182
POTASH SOAP	138.9832	4.367468	1.705984	145
ENCAPSULATED DELTA ENDOTOXIN OF BACILLUS THURINGIENSIS VAR. KURSTAKI IN KILLED PSEUDOMONAS FLUORESCENS	84.05638	54.85174		139
FENAMIPHOS	95.48263			95
BENTAZON, SODIUM SALT	95.09195			95
ETHEPHON	84.62722	5.205174	4.310678	94
LINDANE		6.30168	77.41996	84
ENDOSULFAN	8.692873	51.5497	19.66	80
PETROLEUM DISTILLATES, AROMATIC	8.73734	32.81436	20.58798	62
DIETHATYL-ETHYL	60.00081			60
METHAMIDOPHOS	54.15344			54
GIBBERELLINS	14.6719	15.3269	14.69804	45
TAU-FLUVALINATE	28.60579	11.3695	1.928192	42
MYROTHECIUM VERRUCARIA, DRIED		36.28548		36

FERMENTATION SOLIDS & SOLUBLES				
FENARIMOL	5.823707	13.32097	16.59667	36
BROMOXYNIL OCTANOATE		32.77108		33
SETHOXYDIM	28.03878	0.61335	2.80386	31
AZADIRACHTIN	6.289033	17.52943	5.873242	30
PYRETHRINS	8.030477	8.557481	11.2013	28
MEFENOXAM, OTHER RELATED		11.75421	10.60247	22
ROTENONE	6.692064	6.252915	9.334419	22
ROTENONE, OTHER RELATED	6.692064	6.252915	9.334419	22
MCPA, DIMETHYLAMINE SALT	10.7562	9.219668		20
ETHOPROP	19.02801			19
TRIADIMEFON	2.3875	9.28285	5.770325	17
ALUMINUM PHOSPHIDE	3.196875	7.871875	5.878125	17
SULFOTEP	8.925	3.54375	1.96875	14
KINOPRENE	8.076173	6.068264		14
(S)-KINOPRENE			13.91434	14
PROPAMOCARB HYDROCHLORIDE	13.31301			13
METHIOCARB	1.5	4.14375	6.825	12
AVERMECTIN	6.561536	4.096372	0.273803	11
CLARIFIED HYDROPHOBIC EXTRACT OF NEEM OIL	10.12095			10
TRALOMETHRIN			9.843239	10
TEBUFENOZIDE			9.783648	10
PHOSPHORIC ACID	2.117903		6.353708	8
POTASSIUM BICARBONATE			6.15	6
STRYCHNINE	0.035	4.6425	0.2115	5
BIFENTHRIN		1.578302	2.646066	4
ALKYLARYL	0.937125		2.811375	4
POLYOXYETHYLENE GLYCOL PHOSPHATE ESTER				
AZINPHOS METHYL	2.5		1	4
BACILLUS THURINGIENSIS (BERLINER), SUBSP. KURSTAKI, SEROTYPE 3A,3B	0.9	0.896	0.768	3
DIENOCHLOR	0.36119	0.42712	1.733674	3
CARBOPHENOTHION		2.147947		2
LAMBDA CYHALOTHRIN			2.085324	2
CHLORSULFURON	1.00545		0.928125	2
METHYL PARATHION			1.919096	2
(S)-CYPERMETHRIN	1.164934		0.323429	1
COPPER SULFATE (PENTAHYDRATE)	0.064272	0.425812	0.899811	1
MANGANESE SULFATE		0.687477	0.458318	1
BEAUVERIA BASSIANA STRAIN GHA		0.721217	0.328288	1
TRIFORINE	0.534006	0.214906		1
BACILLUS THURINGIENSIS (BERLINER), SUBSP.	0.02584	0.228		0
AIZAWAI, GC-91 PROTEIN				

BENDIOCARB		0.19	0
ZINC SULFATE	0.08839	0.058927	0
METHYL PARATHION, OTHER RELATED		0.101005	0
CHLORMEQUAT CHLORIDE	0.023494	0.050126	0
BACILLUS THURINGIENSIS (BERLINER)	0.016		0
DIPHACINONE	0.005	0.005	0
AMPELOMYCES QUISQUALIS	0.0025	0.000507	0

Table 3. List of pesticides and breakdown products the TAG reprioritized in 1999-2000 and targeted for air monitoring in Lompoc. These were chosen from the pesticides for which at least 90 reported pounds were applied in the Lompoc area for 1996-1998. Each pesticide on the initial list was separately ranked for pounds applied, vapor pressure, and toxicity. The top 17 from each of the three categories were combined to make up the list below.

Pesticide	Breakdown Product	Why not on candidate lists?
Acephate	Methamidophos ¹	
Anilazine		
Benomyl	Methyl 2-benzimidazole carabamate (MBC)²	Difficult method, single method
Chlorothalonil		
Chlorpyrifos	Oxygen analog	
Chlorthal-dimethyl	Monomethyl and tetrachloroterephthalic acid (TPA, MTP)	Single method
Cycloate		
Diazinon	Oxygen analog	
Dicloran		
Dicofol		
Dimethoate	Oxygen analog	
Disulfoton	Disulfoton oxygen analog	Single method
EPTC		
Ethalfuralin		
Ethephon		
Fonofos	Oxygen analog	
Fosetyl-Al		Difficult method, low toxicity
Glyphosate		Single method, low toxicity
Iprodione		
Malathion	Oxygen analog	
Mancozeb	Ethylene thiourea	Difficult method
Maneb	Ethylene thiourea	Difficult method
Mefenoxam		
Methomyl		
Metolachlor		
Naled	DDVP (dichlorvos)	

¹ Methamidophos is also a pesticide active ingredient that is applied in the Lompoc area.

² The compounds shown in bold are those not included as candidate pesticides for which to develop methods. See the reason shown in the last column.

Oxamyl		
Oxydemeton-methyl		
PCNB		
Permethrin		
Propyzamide		
Simazine	Deethyl simazine, diaminochlorotriazine	Single method
Sulfur		Single method, low toxicity
Sulfuryl fluoride		Single method, study design does not include its residential structural uses
Thiodicarb		
Thiophanate-methyl	Methyl 2-benzimidazole carbamate (MBC)	Difficult method, single method
Trifluralin		
Vinclozolin		

Table 4. Group 1 – List of Candidate Compounds for a Multiresidue Air Sampling Scheme (analysis by gas chromatography, UCD). Samples will be collected from late May through early August.

Pesticide (Active Ingredient)	Breakdown product
Chlorothalonil	
Chlorpyrifos	Chlorpyrifos oxon
Chlorthal-dimethyl	
Cycloate	
Diazinon	Diazinon oxon
Dicloran	
Dicofol	
Dimethoate	Dimethoate oxon
EPTC	
Ethalfuralin	
Fonofos	Fonofos oxon
Iprodione	
Malathion	Malathion oxon
Mefenoxam	
Metolachlor	
Naled	
Oxydemeton-methyl	
PCNB	
Permethrin	
Propyzamide	
Simazine	
Trifluralin	
Vinclozolin	

Table 5. Group 2 – List of Candidate Compounds for Multiresidue Air Sampling Scheme (analysis by liquid chromatography/mass spectroscopy, Battelle). Samples will be collected in September.

Pesticide (Active Ingredient)	Breakdown product
Acephate	Methamidophos ³
Anilazine	
Benomyl	
	DDVP (from Naled)
Ethephon	
Maneb	
Methomyl	
Oxamyl	
Thiodicarb	
Thiophanate-methyl	

³ Methamidophos is also a pesticide active ingredient that is applied in the Lompoc area.

Table 6. Pounds of candidate pesticides applied in the Lompoc study area, 1996-1998.

PESTICIDE	1996	1997	1998	Total
ACEPHATE	2,921	2,676	2,382	7,979
ANILAZINE	389	178	131	697
BENOMYL	365	172	255	792
CHLOROTHALONIL	3,593	1,243	1,843	6,679
CHLORPYRIFOS	4,553	4,670	2,917	12,139
CHLORTHAL-DIMETHYL	6,804	6,601	3,527	16,932
CYCLOATE	215	294	288	798
DIAZINON	525	903	700	2,128
DICLORAN	2,292	2,063	1,896	6,251
DICOFOL	288	21	20	329
DIMETHOATE	200	536	601	1,337
EPTC	81	39	65	186
ETHALFLURALIN	638	381	385	1,404
ETHEPHON	85	5	4	94
FONOFOS	570	282	220	1,072
IPRODIONE	4,964	4,682	4,535	14,181
MALATHION	1,274	509	358	2,140
MANEB	7,368	8,785	9,130	25,283
MEFENOXAM	0	400	359	758
METHAMIDOPHOS*	54	0	0	54
METHOMYL	1,932	3,022	974	5,929
METOLACHLOR	407	484	698	1,589
NALED	28	231	515	773
OXAMYL	1,188	749	461	2,398
OXYDEMETON-METHYL	729	989	883	2,601
PCNB	55	550	2,834	3,439
PERMETHRIN	2,151	2,128	1,723	6,002
PROPYZAMIDE	2,124	2,587	2,294	7,005
SIMAZINE	859	0	41	900
THIODICARB	1,395	1,761	75	3,231
THIOPHANATE-METHYL	336	491	834	1,660
TRIFLURALIN	183	199	174	557
VINCLOZOLIN	905	870	900	2,674
Total	49,470	48,500	42,023	139,994

*This is the breakdown product of acephate as well as a pesticide active ingredient.

Table 7. Pounds of candidate pesticides applied in the Lompoc study area by month, 1996-1998.

PESTICIDE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Total
ACEPHATE	95	416	993	1006	1098	1168	1114	1161	809	112	4	2	7979
ANILAZINE	0	0	6	4	71	134	0	2	48	279	155	0	697
BENOMYL	1	62	51	15	102	94	80	98	94	64	103	30	792
CHLOROTHALONIL	138	105	126	266	510	802	613	902	921	1132	784	380	6679
CHLORPYRIFOS	705	462	881	1068	1048	1166	1525	1597	1658	749	610	670	12139
CHLORTHAL-DIMETHYL	1576	1824	1974	1751	1895	2285	1866	1638	578	470	455	620	16932
CYCLOATE	21	56	39	95	30	41	73	128	129	78	56	52	798
DIAZINON	3	8	105	108	259	418	445	310	35	133	305	0	2128
DICLORAN	41	84	101	221	618	852	847	1326	1188	962	8	2	6251
DICOFOL	0	0	0	0	6	0	105	197	20	0	0	0	329
DIMETHOATE	28	31	85	159	232	148	211	195	95	100	2	51	1337
EPTC	0	0	0	0	186	0	0	0	0	0	0	0	186
ETHALFLURALIN	0	0	74	29	1270	31	0	0	0	0	0	0	1404
ETHEPHON	0	0	0	0	0	3	6	1	65	19	0	0	94
FONOFOS	0	172	130	116	320	114	90	0	0	64	66	0	1072
IPRODIONE	299	677	1263	1423	1751	1829	2010	1900	1750	604	514	163	14181
MALATHION	0	42	0	77	4	35	876	935	121	42	9	0	2140
MANEB	414	1548	3390	2905	3446	3174	2936	2907	3059	1123	153	229	25283
MEFENOXAM	35	11	0	0	0	122	382	5	5	5	2	191	758
METHAMIDOPHOS*	0	0	0	0	0	0	20	30	5	0	0	0	54
METHOMYL	3	1	15	57	404	663	1126	1514	1527	558	52	9	5929
METOLACHLOR	0	0	0	0	891	698	0	0	0	0	0	0	1589
NALED	26	35	49	9	50	150	104	77	184	74	16	0	773
OXAMYL	0	0	0	30	25	199	344	600	602	542	55	0	2398
OXYDEMETON-METHYL	63	108	182	283	332	287	298	418	348	158	57	68	2601
PCNB	156	245	448	461	392	437	576	550	80	66	29	0	3439
PERMETHRIN	44	102	374	423	702	744	867	924	956	634	182	50	6002
PROPYZAMIDE	925	636	911	608	751	663	781	818	117	8	173	615	7005
SIMAZINE	41	0	0	0	0	380	390	89	0	0	0	0	900
THIODICARB	64	66	148	69	210	327	426	518	875	416	65	47	3231
THIOPHANATE-METHYL	93	19	49	44	188	262	230	158	178	134	93	211	1660
TRIFLURALIN	0	0	0	25	459	73	0	0	0	0	0	0	557
VINCLOZOLIN	410	152	86	51	126	36	101	223	269	205	414	601	2674
Total	5180	6863	11480	11304	17377	17334	18440	19221	15714	8730	4361	3990	139994

*This is the breakdown product of acephate as well as a pesticide active ingredient.

Table 8. For each pesticide, final screening levels and recommended responses.

Final Health Screening Level (SL)	Ambient Air Concentration⁴	Recommended Response⁵
Acute: to be determined ⁶	Maximum 24-hour air concentration at any site < acute SL	Not necessarily a health concern. No immediate response. May still merit further analysis.
Acute	Maximum 24-hour air concentration at any site > acute SL	Not necessarily a health concern. However, initiate interim regulatory action, a more refined analysis, or both.
Subchronic: to be determined	Maximum 8-day average of 24-hr air concentrations at any site during monitoring < subchronic SL	Not necessarily a health concern. No immediate response. May still merit further analysis.
Subchronic	Maximum 8-day average of 24-hour air concentrations at any site during monitoring > subchronic SL	Not necessarily a health concern. However, initiate interim regulatory action, a more refined analysis, or both.
Chronic: to be determined	Annual average concentration < final chronic SL	Not necessarily a health concern. No immediate response.
Chronic	Annual average concentration > final chronic SL	DPR will conduct further analysis.

⁴ Ambient air concentrations will be calculated as described in Section 8.1 of this plan.

⁵ A more refined analysis could include, but not be limited to, more air monitoring, and a more refined risk analysis. Regulatory actions could include, but not be limited to, permit conditions for restricted materials, statewide regulations, and label changes.

⁶ See Appendix C for a brief description of the process TAG toxicologists will use to determine acute, subchronic and chronic final screening levels.

Table 9. Summary of field sampling parameters and minimum chemical analytical parameters for the pesticides monitored in Lompoc during late May through early August and in September 2000.

Analyte

	UC Davis Trace Analytical Lab	Battelle Memorial Inst. Lab
Sorbent Tube Adsorbent	XAD-4 resin	XAD-4 resin
Analytical Method ⁷	GC	LC
Extraction Solvent	Ethyl acetate	To be determined
Detector	FPD and MSD	ESI/MS/MS
Trapping Efficiency	See Table 17	To be determined
Storage Stability	See Table 17	To be determined
Flow Rate (L/min)	15	15

⁷ See respective appendices for details.

Table 10. Group 1 -- List of Candidate Compounds for a Multiresidue Air Sampling Scheme (analysis by gas chromatography at UCD). Monitoring is planned for late May through early August 2000.

Pesticide (Active Ingredient)	Breakdown product	Detection Limit (ng/m³)	Limit of Quantitation (ng/m³)	Preliminary Screening level (ng/m³)
Chlorpyrifos	Chlorpyrifos oxon	0.76	4	1,000
Chlorthal-dimethyl		0.28	1	4,700
Chlorothalonil		1.4	7	2,300
Cycloate		1.8	9	16,000
Diazinon	Diazinon oxon	0.72	4	300
Dicloran		1.3	6	82,000
Dicofol		1.3	7	3,900
Dimethoate	Dimethoate oxon	0.56	3	330
EPTC		0.62	3	41,000
Ethalfuralin		0.60	3	79
Fonofos	Fonofos oxon	0.66	3	6,600
Iprodione		1.5	8	160
Malathion	Malathion oxon	0.82	4	4,600
Mefenoxam		0.60	3	200,000
Metolachlor		0.58	3	250,000
Naled		0.96	5	6,600
Oxydemeton-methyl*				410
PCNB		0.84	4	27
Permethrin		1.4	7	380
Propyzamide		1.7	8	450
Simazine		0.60	3	58
Trifluralin		1.5	8	910
Vinclozolin		0.38	2	39,400

*Oxydemeton-methyl cannot be analyzed as part of this multi-pesticide analysis since it requires a separate analysis. Therefore, separate samples will be collected the last two weeks of this sampling period and analyzed for oxydemeton-methyl using a separate single-pesticide analytical method.

Table 11. Group 2—List of Candidate Compounds for Multiresidue Air Sampling Scheme (liquid chromatography/mass spectroscopy analysis at Battelle). Monitoring is planned for September 2000.

Pesticide (Active Ingredient)	Breakdown product	Target limit of quantitation (ng/m³)	Preliminary screening level (ng/m³)
Acephate		5	800
Acephate	Methamidophos*	5	50
Anilazine		5	1,300
Benomyl		5	1,700
	DDVP (from Naled)	5	20
Ethephon		5	59,000
Maneb		5	160
Methomyl		5	26,000
Oxamyl		5	660
Thiodicarb		5	370
Thiophanate-methyl		5	3,400

*Methamidophos is also a pesticide active ingredient that is applied in the Lompoc area.

Table 12. Some physical and chemical properties of the candidate pesticides that may be monitored in Lompoc during late May through early August and in September 2000.

Analyte	Molecular Weight (g/mole)	Water Solubility ^a (ppm)	Vapor Pressure ^b (mmHg)	Hydrolysis Half-life ^c (days)	Aerobic Soil Half-life ^d (days)	Photolysis Half-life ^e (days)
Acephate	183.2	818,000	2.66E-07	169	3	8.68
Anilazine	275.5	8	NA ^f	19	1	9.61
Benomyl	290.3	NA	3.73E-08	0.06	0.79	0.22
Chlorothalonil	265.9	1.2	2.40E-04	49 ^g	35	74
Chlorpyrifos	350.6	1.39	2.21E-05	72.1	NA	10
Chlorthal-dimethyl	303.9	0.5	2.50E-04	36 ^g	0.26	168 ^g
Cycloate	215.4	95	1.60E-03	30	43	36.5
Diazinon	304.3	60	8.98E-05	138	40	2.55
Dicloran	207.0	6	1.97E-06	72 ^g	549	4.38
Dicofol	370.5	NA	3.90E-06	2.74	66.4	60.2
Dimethoate	229.2	39,800	1.85E-06	68	2	66.7
EPTC	189.3	345	2.64E-02	30 ^g	42	NA
Ethalfuralin	333.3	2.93	8.80E-05	33	45	21.1
Ethephon	144.5	NA	NA	2.43	7.5	NA
Fonofos	246.3	17	3.04E-04	432	80	25.8
Iprodione	330.2	12	1.00E-07	5	64	13.7
Malathion	330.3	125	2.30E-05	6	2	174
Maneb	265.3	417	NA	NA	NA	NA
Metenoxam	279.3	26000	2.48E-05	1000	60.2	30 ^g
Methomyl	162.2	547,000	4.90E-05	30 ^g	46	33
Metolachlor	283.8	492	3.14E-05	200 ^g	26	37
Naled	380.8	2,000	2.00E-04	0.68	3	5
Oxamyl	219.3	284,000	3.84E-07	8	10.7	4.8
Oxydemeton-methyl	246.3	NA	3.83E-05	40	6	73.7
PCNB	295.3	0.39	7.74E-05	180 ^g	80.2	28.5
Permethrin	391.3	0.07	2.15E-08	42	10.5	289
Propyzamide	256.1	13	4.35E-07	42 ^g	392	113
Simazine	201.7	6	2.21E-08	28 ^g	110	11.1
Thiodicarb	354.5	23.5	2.00E-05	13	3.6	36.9
Thiophanate-methyl	342.5	25	1.73E-05	41	13.7	13.7
Trifluralin	335.3	0.3	1.04E-04	30	169	41

Vinclozolin	286.1	3	32	1 ^e	28	NA
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^a 9 - 25 °C
^b 20 - 25 °C
^c 19 - 25 °C; pH 6 - 7.5
^d Averaged over different soil types
^e Soil photolysis
^f Not available
^g No reaction occurred during the study. The half-life is greater than the value listed which represents the length of the study.

Table 13. Township, range and sections used to define the agricultural boundary for the Lompoc air monitoring studies. *

Meridian	Township	Range	section
S	06N	34W	1
S	06N	34W	2
S	06N	34W	3
S	06N	34W	4
S	06N	34W	5
S	06N	34W	6
S	06N	35W	1
S	07N	34W	19
S	07N	34W	20
S	07N	34W	21
S	07N	34W	22
S	07N	34W	23
S	07N	34W	24
S	07N	34W	25
S	07N	34W	26
S	07N	34W	27
S	07N	34W	28
S	07N	34W	29
S	07N	34W	30
S	07N	34W	31
S	07N	34W	32
S	07N	34W	33
S	07N	34W	34
S	07N	34W	35
S	07N	34W	36
S	07N	35W	20
S	07N	35W	21
S	07N	35W	22
S	07N	35W	23
S	07N	35W	24
S	07N	35W	25
S	07N	35W	26
S	07N	35W	27
S	07N	35W	28
S	07N	35W	29
S	07N	35W	32
S	07N	35W	33
S	07N	35W	34
S	07N	35W	35
S	07N	35W	36

*See Figure 3 for agricultural boundaries defined by the above Township-Range-sections.

06N34W06	07N34W19	07N34W20	07N34W21	07N34W22	07N34W23	07N34W24	07N34W25	07N34W26	07N34W27	07N34W28	07N34W29	07N34W30	07N34W31	07N34W32	07N34W34	07N34W35	07N35W20	07N35W22	07N35W23	07N35W24	07N35W25	07N35W26	07N35W29	07N35W35	07N35W36	Grand Total
22 0 4 8 30 90	117 0 0 14 241 201	0 0 0 0 0 0	0 0 0 0 0 0	0 0 0 0 139 11	0 0 0 0 5 0	33 0 7 87 290 392	299 0 12 82 286 0	113 0 47 45 319 171	221 0 37 257 361 120	104 65 31 244 128 475	29 0 16 20 273 1189	1017 157 133 1211 1464 2160	1189 0 53 427 1919 2131	869 62 81 689 657 2021	4 0 0 4 0 0	0 0 3 2 96 5	0 0 0 0 14 0	0 0 0 0 0 0	0 0 0 0 64 0	3 0 18 263 1049 297	336 246 47 670 1049 1198	1490 36 162 1348 1483 1806	74 0 4 94 160 236	193 0 5 81 185 601	1313 4 47 662 2145 3651	
0 5 25 0 2 0 																										

Table 15. This list shows the use and chemical class for each candidate pesticide.

Pesticide (Active Ingredient)	Breakdown Product	Use	Chemical Class
Acephate	Methamidophos ¹	Insecticide	Organophorus
Anilazine		Fungicide	Triazine
Benomyl		Fungicide	Benzimidazole
Chlorothalonil		Fungicide	Chloronitrile
Chlorpyrifos	Chlorpyrifos oxon	Insecticide	Organophosphorus
Chlorthal-dimethyl		Herbicide	Benzoic acid
Cycloate		Herbicide	Thiocarbamate
Diazinon	Diazinon oxon	Insecticide	Organophosphorus
Dicloran		Fungicide	Dinitroaniline
Dicofol		Insecticide	Organochlorine
Dimethoate	Dimethoate oxon	Insecticide	Organophosphorus
EPTC		Herbicide	Carbamate
Ethalfuralin		Herbicide	Dinitroaniline
Ethephon		Plant growth regulator	Ethylene generator
Fonofos	Fonofos oxon	Insecticide	Organophosphorus
Iprodione		Fungicide	Dicarboximide
Malathion	Malathion oxon	Insecticide	Organophosphate
Maneb		Fungicide	Alkylenebis(dithiocarbamate)
Mefenoxam		Fungicide	Phenylamide
Methomyl		Insecticide	Oxime carbamate
Metolachlor		Herbicide	Chloracetanilide
Naled	DDVP (Dichlorvos)	Insecticide	Organophosphate ester
Oxamyl		Insecticide	Oxime carbamate
Oxydemeton-methyl		Insecticide	Organophosphorus
PCNB		Fungicide	Organochlorine
Permethrin		Insecticide	Pyrethroid
Propyzamide		Herbicide	Amide
Simazine		Herbicide	Triazine
Thiodicarb		Insecticide	Oxime carbamate
Thiophanate-methyl		Fungicide	Carbamate
Trifluralin		Herbicide	Dinitroaniline
Vinclozolin		Fungicide	Dicarboximide

¹ Methamidophos is also a pesticide active ingredient that is applied in the Lompoc area.

Table 16. PRELIMINARY INFORMATION: Method Detection Limit (MDL) and Estimated Quantitation Limit (EQL) for the Group 1 analytes (Trace Analytical Laboratory, UC Davis).

	Replicates (pg/μL)								Average	S. D.	MDL (pg/μL)	EQL		
	1	2	3	4	5	6	7	8				(pg/μL)	μg	ng/m ³ *
EPTC	22.3	23.0	22.6	24.0	22.2	23.7	21.8	25.3	23.1	1.1	3.4	17.2	0.069	3.1
Ethalfuralin	26.6	27.2	28.9	28.6	27.0	29.2	28.8	26.6	27.9	1.1	3.4	16.8	0.067	3.0
Trifluralin	28.4	28.7	30.4	29.7	28.0	22.1	30.1	31.3	28.6	2.9	8.6	42.8	0.171	7.6
Cycloate	22.6	24.0	24.7	24.6	22.7	25.1	23.8	33.1	25.1	3.4	10.1	50.6	0.203	9.0
Propyzamide	27.7	28.8	31.0	30.2	28.8	32.2	32.9	37.6	31.2	3.2	9.5	47.3	0.189	8.4
PCNB	25.8	26.9	27.4	27.3	26.8	28.2	28.1	31.2	27.7	1.6	4.8	23.8	0.095	4.2
Simazine	25.9	26.4	26.5	26.2	27.0	28.7	27.9	28.9	27.2	1.1	3.4	17.1	0.068	3.0
Dichloran	27.0	28.7	30.8	29.2	29.6	30.3	29.7	35.2	30.1	2.4	7.2	35.8	0.143	6.4
Vinclozolin	25.3	26.2	26.8	25.6	25.4	26.6	25.5	27.1	26.1	0.7	2.1	10.6	0.043	1.9
Chlorothalonil	17.3	19.0	23.4	22.9	23.4	24.8	23.8	24.0	22.3	2.7	8.0	40.2	0.161	7.1
Mefenoxam	25.3	26.3	24.7	23.5	24.1	24.7	24.0	22.6	24.4	1.1	3.3	16.6	0.067	3.0
Metolachlor	26.0	27.4	28.1	27.1	27.3	28.8	28.8	29.2	27.8	1.1	3.3	16.3	0.065	2.9
Chlorthal-dimethyl	24.3	25.2	24.9	24.6	24.1	25.6	25.0	25.6	24.9	0.5	1.6	8.2	0.033	1.4
Iprodione	25.8	27.2	31.1	29.6	31.6	31.4	30.5	35.0	30.3	2.8	8.5	42.4	0.170	7.5
Dicofol	28.4	31.2	24.8	24.9	24.2	25.0	24.3	27.0	26.2	2.5	7.5	37.3	0.149	6.6
Permethrin	25.7	26.4	27.3	27.0	29.2	25.2	29.4	33.5	28.0	2.7	8.1	40.3	0.161	7.2
Diazinon	24.1	24.6	23.9	22.7	24.8	21.3	21.6	22.9	23.2	1.3	4.0	20.2	0.081	3.6
Naled	24.1	21.9	23.7	21.4	23.0	21.8	18.5	20.7	21.9	1.8	5.4	27.0	0.108	4.8
Fonofos	23.7	23.5	23.6	22.1	23.4	21.1	21.3	20.8	22.5	1.2	3.7	18.5	0.074	3.3
Fonofos Oxon	23.9	24.8	24.7	22.8	24.6	22.2	23.0	23.3	23.6	1.0	3.0	14.9	0.060	2.6
Diazinon Oxon	24.6	26.1	23.9	24.8	25.0	23.3	23.2	23.7	24.3	1.0	2.9	14.7	0.059	2.6
Chlorpyrifos	24.7	26.0	24.3	23.5	26.9	23.0	22.9	23.9	24.4	1.4	4.3	21.6	0.087	3.8
Dimethoate Oxon	25.7	26.4	26.5	24.7	26.4	24.2	24.9	24.8	25.4	0.9	2.7	13.4	0.053	2.4
Dimethoate	24.4	25.4	25.3	23.3	25.5	22.9	23.4	24.0	24.3	1.0	3.1	15.6	0.062	2.8
Malathion	25.0	25.3	26.6	22.8	26.3	23.0	22.9	23.8	24.4	1.5	4.6	23.2	0.093	4.1
Chlorpyrifos Oxon	24.9	26.6	25.8	24.8	26.4	24.4	23.7	24.8	25.2	1.0	3.1	15.3	0.061	2.7
Malathion Oxon	26.3	26.3	25.2	25.5	26.6	25.4	24.4	25.0	25.6	0.8	2.3	11.4	0.045	2.0
Oxydemeton-methyl**														5.0

*Flow rate = 15 L/min **This data was developed as part of the Phase One project (Okumura, 1999).

Table 17. Storage stability and trapping efficiency data from UCD for Group 1 candidate pesticides and breakdown products.

Compound	Detector	Storage Stability (% recovery)		Trapping (% recovery)			Notes
		Day 0	Day 31	Wool	Resin	Total	
Chlorothalonil	MSD	107*	100*	*	*	78*	1
Chlorpyrifos	FPD	105*	93*	*	*	105*, **	1, 7
Chlorpyrifos Oxon	FPD	86	98	7.9	50	58	2
Chlorthal-dimethyl	MSD	97	92	25	79	04	4
Cycloate	MSD	89	113	0	37	37	4
Diazinon	FPD	102*	92*	*	*	117*	1
Diazinon Oxon	FPD	88	98	0	89	89	2
Dichloran	MSD	88	85	26	67	93	4
Dicofol	MSD	78	74	61	41	103	3
Dimethoate	FPD	105*	95*	*	*	133*	1
Dimethoate Oxon	FPD	89	96	21	69	90	2
EPTC	MSD	91	107	0	53	53	3
Ethalfuralin	MSD	83	96	0	60	60	4
Fonofos	FPD	97*	89*	*	*	102*	1
Fonofos Oxon	FPD	87	95	0	87	87	2
Iprodione	MSD	88	89	77	5	82	5
Malathion	FPD	90	99	27	58	86	2
Malathion Oxon	FPD	88	105	34	71	104	2
Mefenoxam	MSD	91	91	7.8	83	91	3
Metolachlor	MSD	93	90	15	77	93	4
Naled	FPD	N/A	108	2.4	69.2	74	6
Oxydemeton-methyl	FPD	112*	99*	*	*	102*	1
PCNB	MSD	87	83	0	93	93	4
Permethrin	MSD	107*	98*	*	*	110*	1
Propyzamide	MSD	85	87	0	77	77	3
Simazine	MSD	95	92	69	21	90	7
Trifluralin	MSD	85	95	0	77	77	3
Vinclozolin	MSD	93	92	6.8	82	89	3

1: * Indicates Storage Stability (for days 0 and 30) and Trapping were completed during Phase One for that compound (Okumura, 1999).

2: Trapping Experiments were run using Mix #2

3: Trapping Experiments were run using Mix #3

4: Trapping Experiments were run using Mix #4

5: ** Indicates that chlorpyrifos and its oxygen analog detected in the control sample, cannot determine relative proportions

6: Mourer, C.R., G. Hall, T. Shibamoto. 1994. Method Development for Naled and Dichlorovos in Air Samples Using XAD-4 as a Trapping Medium. Report to the California Air Resources Board, April 1995. Storage stability tests were run for 21 days; no data were available for day 0.

7: Trapping Experiments were run using Mix #5 and Heat Tape

Figure 1. Location of Lompoc sampling sites and weather station for pesticide monitoring.

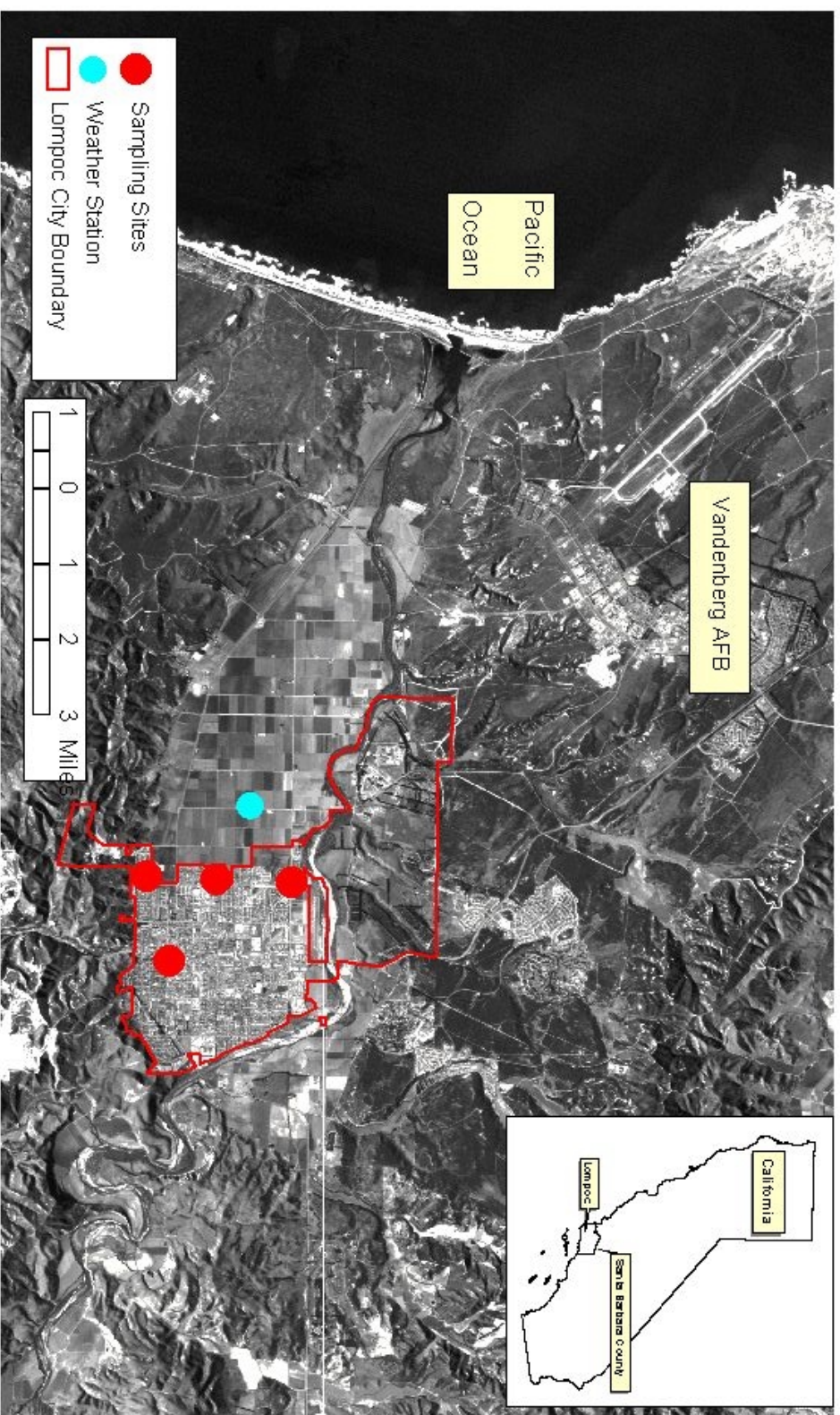


Figure 2. The percentage of time the wind blows from various directions during the months of May through October. Compiled from weather data collected during 1992-1994 at the H Street weather station located in downtown Lompoc.

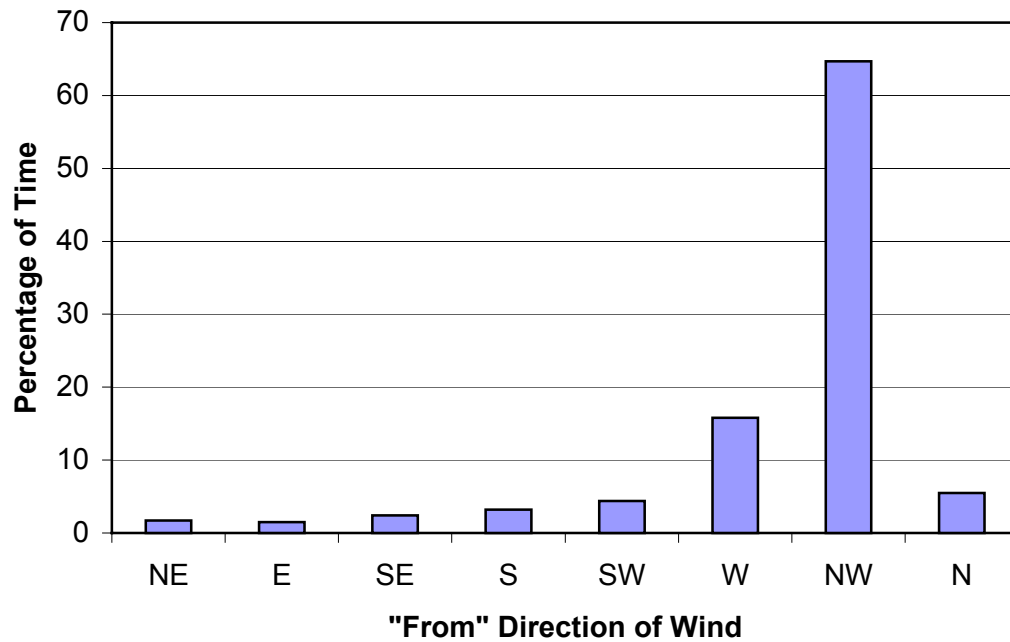


Figure 3. Township, range, and sections showing the extent of the agricultural area within which pesticide use will be monitored.

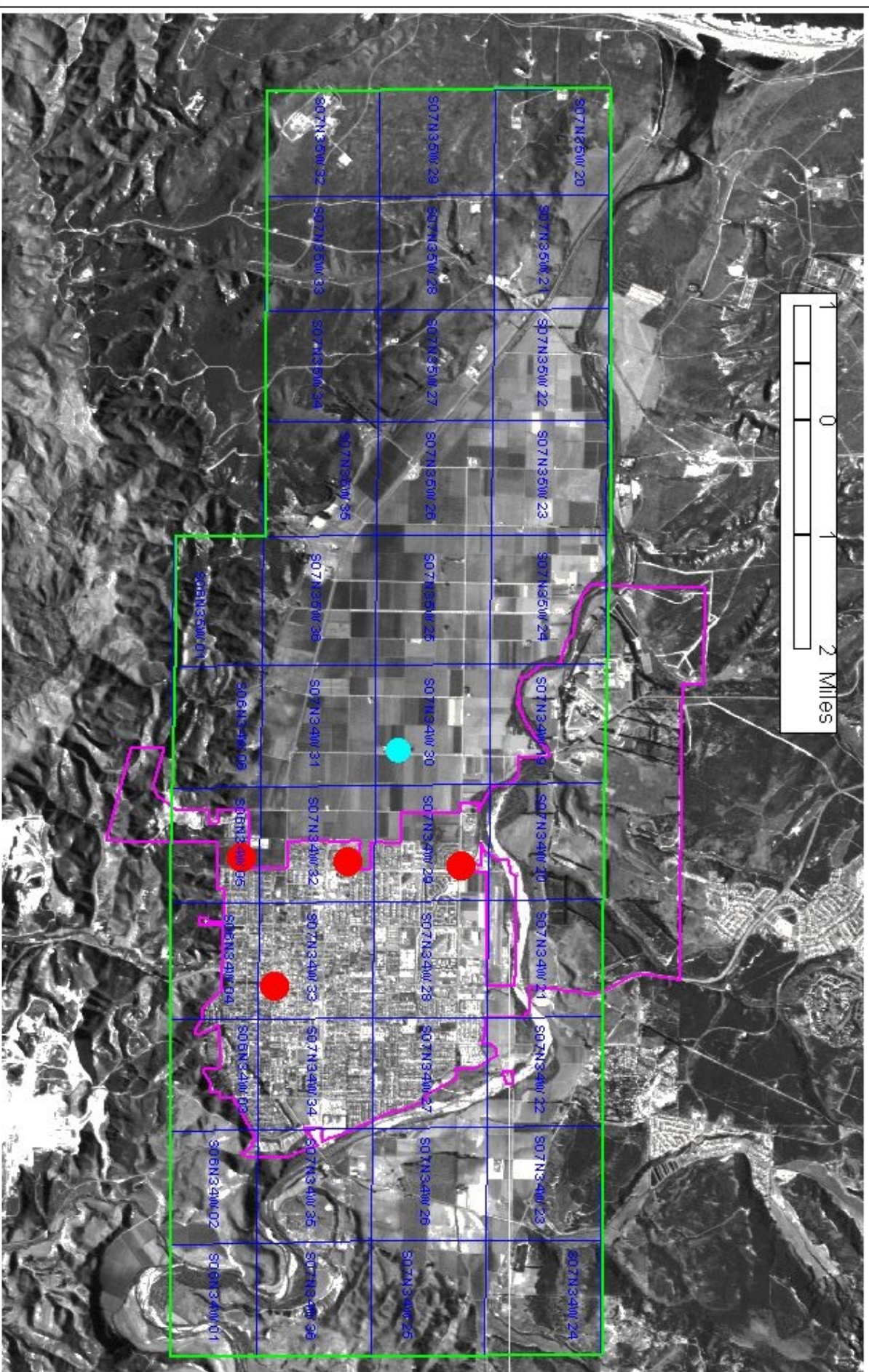


Figure 4. Township, range, and section designations in the Lompoc Valley.

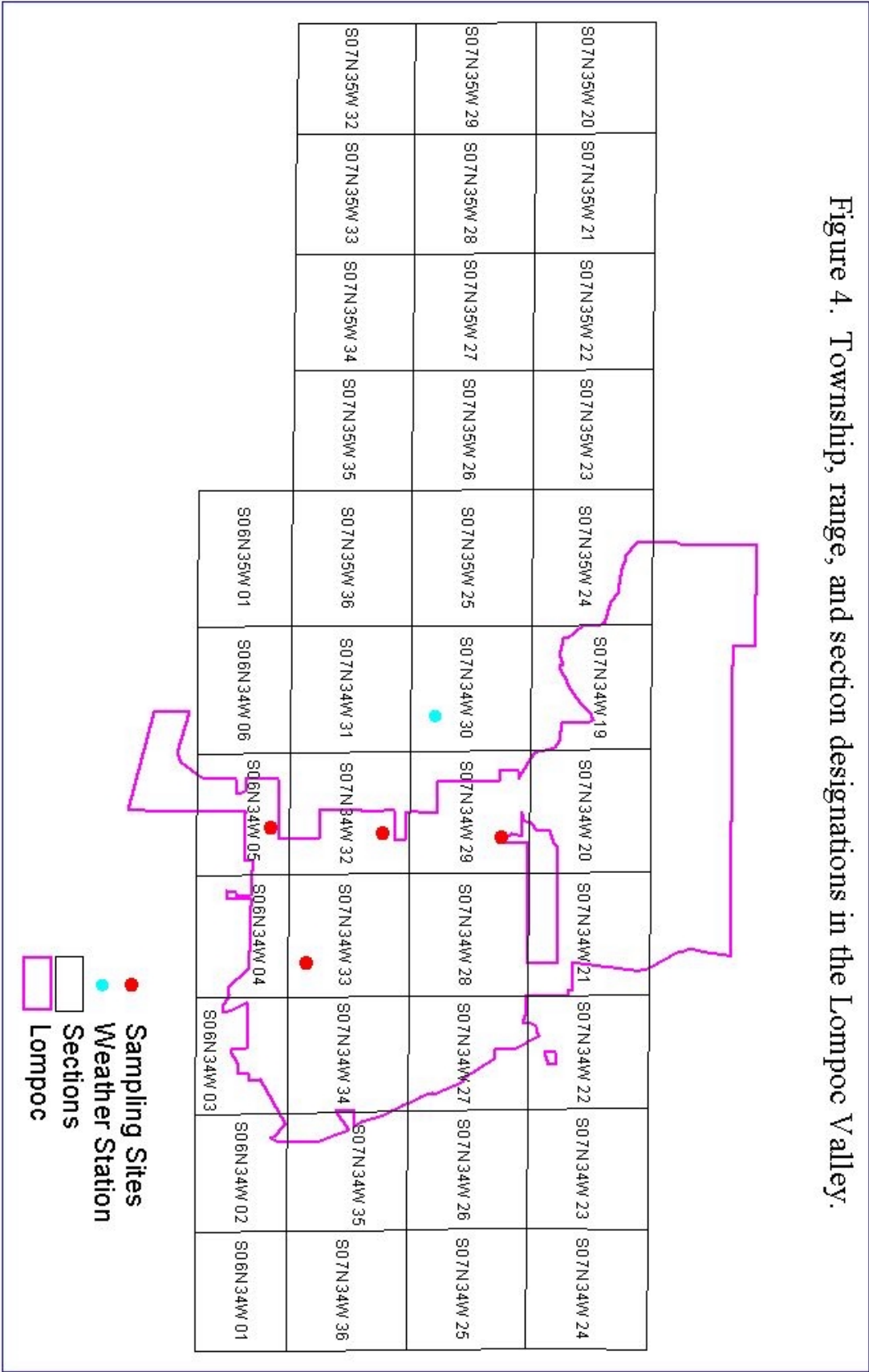


Figure 5. Project Organization

